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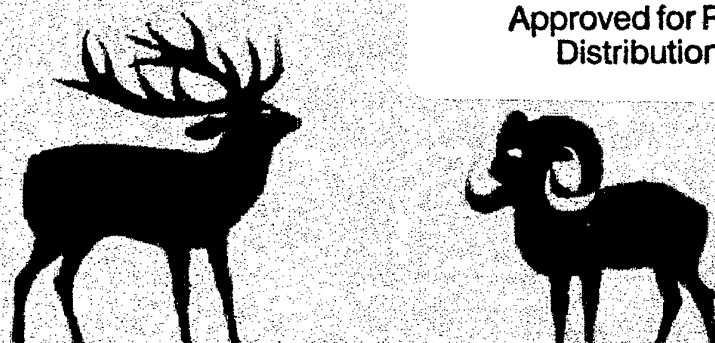
# **Excited States of Transition Elements**

**6-11 June 2001**

**Wroclaw - Łądek Zdrój, Poland**



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**ESTE 5**  
**5<sup>th</sup> International Conference on Excited States of Transition Elements**  
**6-11 June 2001**  
**Wrocław - Łądek Zdrój, Poland**

**SCHEDULE**

**Wednesday, June 6**

**15:30 – Buss departure from Wrocław to Łądek Zdrój**

**17:30 – Arrival to Łądek Zdrój and lodgings**

**18:00 – 19:00 – Dinner**

**19:30 – 21:00 Welcome Cocktail**

**Thursday, June 7**

**8:00 – 8:50 Breakfast**

**8:50 – Opening**

**Chairman: Georges Boulon**

**9:00 – 9:45 – Renata Reisfeld - *Nanosized semiconductor particles in glasses prepared by the sol gel method: their optical properties and potential uses***

**9:45 – 10:30 – Jean Claude Krupa - *High energy luminescence excitation of rare earth doped compounds***

**10:30 – 11:15 – Marco Bettinelli - *Optical spectroscopy of nanocrystalline  $Y_2O_3:Er^{3+}$  prepared by different synthesis techniques***

**11:15 – 11:25 Coffee break**

**Chairman: Pierre Porcher**

**11:25 – 12:10 – Vladislav Zolin - *From molecular engineering to molecular nanoelectronics***

**12:10 – 12:55 – Andreas Meijerink - *Nano sense and nonsense***

**12:55 – 13:15 – Pieter Dorenbos - *Spectroscopy of 5d-levels of  $Ce^{3+}$  in inorganic compounds***

**13:15 – 15:00 – Lunch**

**Chairman: Marian Elbanowski**

**15:00 – 15:30 – Andrzej Suchocki - *High-pressure luminescence study of  $LiNbO_3:MgO,Cr$  and  $La_3Lu_2Ga_3O_{12}:Cr,Nd$  crystals***

**15:30 – 16:00 – Konstantin Pukhov - *Multiphonon sideband intensities in RE ions in crystals***

**16:00 – 16:30 – Olimkhon Alimov - *Up-conversion fluorescence dynamics from the dynamically splitted high-lying excited state of cluster centers in the  $CaF_2$  neodymium doped crystal***

**16:30 – 16:45 Coffee break**

**Chairman: Johann Heber**

**16:45 – 17:15 – Oliver Wenger - *Chemical tuning of transition metal upconversion properties***

**17:15 – 17:45 – Markus Pollnau - *Decorrelation of luminescence signals in fractional energy-transfer upconversion***

**17:45 – 18:15 – Michał Malinowski - *Upconversion processes in holmium activated laser crystals***

**18:15 – 19:00 – Dinner**

**19:00 – 21:00 – Poster Session**



**Friday, June 8**

**8:00 – 8:50 Breakfast**

**Chairman: Gilberto Fernandes de Sá**

**9:00 – 9:45** – Stefan Kueck - *Spectroscopy and laser characteristics of Cr<sup>2+</sup>-doped chalcogenide crystals - Overview and recent results*

**9:45 – 10:30** – Marek Grinberg - *Inhomogeneous broadening of the Cr<sup>3+</sup> sites in LiTaO<sub>3</sub> congruent crystal*

**10:30 – 11:15** – Czesław Koepke - *Excited state spectroscopy of chromium ions in various valence states in glasses*

**11:15 – 11:30 Coffee break**

**Chairman: Oscar Malta**

**11:30 – 12:15** – Brian G. Wybourne - *Relativistic effects in lanthanides and actinides*

**12:15 – 13:00** – Lidia Smentek - *Relativistic model of energy transfer in rare earth doped materials*

**13:00 – 13:30** – Roberto Acevedo - *Spectral intensities in cubic systems*

**13:30 – 14:30 Lunch**

**14:30 – 19:00 – Excursion**

**19:30 – 21:00 – Dinner in a grill-room (a cottage close to the hotel)**

**Saturday, June 9**

**8:00 – 8:50 Breakfast**

**Chairman: Renata Reisfeld**

**9:00 – 9:45** – Johann Heber - *The rare-earth centers in CsCdBr<sub>3</sub>*

**9:45 – 10:30** – Georges Boulon - *Search of optimized trivalent ytterbium doped-inorganic crystals for laser applications*

**10:30 – 11:15** – Jorma Hölsä - *Role of defect states in persistent luminescence materials*

**11:15 – 11:25 Coffee break**

**Chairman: Alexander A. Kaminskii**

**11:25 – 12:10** – Marek Godlewski - *Mn<sup>2+</sup> intra-shell recombination in quantum dots of II-VI compounds*

**12:10 – 12:55** – John M. Zavada - *Thermal quenching characteristics of luminescence from RE ions in GaN thin films*

**12:55 – 13:40** – Tom Gregorkiewicz - *Optical storage and other effects revealed in Si: Er by two-color spectroscopy with a free-electron laser*

**13:40 – 15:00 Lunch**

**Chairman: Andreas Meijerink**

**15:00 – 15:30** – Nikolay A. Kulagin - *Ab initio theory of the electronic structure and levels schemes of nl-ions in solids and clusters*

**15:30 – 16:00** – Gilberto Fernandes de Sa – *Design of highly luminescent lanthanide coordination complexes: Synthesis and applications*

**16:00 – 16:15 Coffee break**

**Chairman: Gerd Meyer**

**16:15 – 16:45** – Marek Pietraszkiewicz - *Highly luminescent lanthanide complexes based on dendrimeric phosphineoxides*

**16:45 – 17:15** – Claudia Wickleder - *Luminescence of BiB<sub>3</sub>O<sub>6</sub>: Eu<sup>3+</sup>*

**18:00 – 19:00 – Dinner**

**20:00 – Bonfire**

**Sunday, June 10**

<b>8:00 – 8:45 Breakfast</b>
<b>Chairman: Brian G. Wybourne</b>
9:00 – 9:45 – Oscar L. Malta - <i>Overlap polarizability of a chemical bond: a scale of covalency and application to lanthanide compounds</i>
9:45 – 10:30 – Marina N. Popova - <i>Crystal-field levels, hyperfine structure, and relaxation processes in CsCdBr:Pr<sup>3+</sup></i>
10:30 – 11:15 – Gerd Meyer - <i>Rare earth's halides weight exciting oxidation states</i>
<b>11:15 – 11:30 Coffee break</b>
<b>Chairman: Michał Malinowski</b>
11:30 – 12:00 – Lothar Schwarz - <i>Nonstoichiometric potassium lanthanum double phosphates</i>
12:00 – 12:30 – Stefan Lis - <i>Luminescence spectroscopy of lanthanide(III) ions in solution</i>
12:30 – 13:00 – Nikolai V. Gaponenko - <i>Enhanced luminescence of lanthanides from xerogel solids embedded in porous anodic alumina</i>
<b>13:00 – 15:00 Lunch</b>
<b>Chairman: Jorma Hölsa</b>
15:00 – 15:20 – Yannick Guyot - <i>Spectral and dynamic study of the broad band UV 4f<sup>2</sup>5d → 4f<sup>3</sup> emission in Nd-doped double sodium yttrium fluoride crystals</i>
15:20 – 15:40 – Philippe Boutinaud - <i>Anti-Stokes luminescence and site selectivity in La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>:Pr<sup>3+</sup></i>
15:40 – 16:00 – Laetitia Laversenne - <i>Growth of rare earth concentration gradient crystal fibers and analyse of dynamical processes of laser resonant transitions in RE-doped Y<sub>2</sub>O<sub>3</sub> (RE= Yb<sup>3+</sup>, Er<sup>3+</sup>, Ho<sup>3+</sup>)</i>
<b>16:00 – 16:15 Coffee break</b>
<b>Chairman: Marina Popova</b>
16:15 – 16:35 – Eugeniusz Zych - <i>Rare earth-doped Lu<sub>2</sub>O<sub>3</sub> based X-ray phosphors</i>
16:35 – 16:55 – Luís António Dias Carlos - <i>Fine-tuning of the chromaticity of the emission colour of organic/inorganic hybrids incorporating Eu<sup>3+</sup>, Tb<sup>3+</sup> and Tm<sup>3+</sup></i>
16:55 – 17:15 – Elena Seregina - <i>Energy transfer between UO<sub>2</sub><sup>2+</sup> and Eu<sup>3+</sup> in POCl<sub>3</sub>-SnCl<sub>4</sub> Solutions</i>
<b>19:30 – Conference Dinner</b>

**Monday, June 11**

**8:00 – 8:45 Breakfast**

**Chairman: Janina Legendziewicz**

**9:00 – 9:45** – Pierre Porcher - *Spectroscopic and magnetic observables in 4f-3d mixed compounds: relationship to the structure*

**9:45 – 10:30** – Alexander A. Kaminskii - *Stimulated Raman spectroscopy of k(3)-active  $\text{Ln}^{3+}$ -doped laser crystals*

**10:30 – 11:00** – Andrei Kuzmin - *Laser and spectral properties of Yb doped KYW microchip laser*

**11:00 – 11:15 Coffee break**

**Chairman: Jean Claude Krupa**

**11:15 – 11:30** – Janina Legendziewicz - *Spectroscopy of nanometer – range media and mixed lanthanide  $\text{Ln}\beta_3\text{L}$  compounds. Their application perspectives:*

**11:30 – 11:45** - Wiesław Stręk - *Nanometric luminophors based on Eu and Tb doped compounds*

**11:45 – 12:00 – Closing**

**12:00 – 13:00 Lunch**

**13:00 – Buss departure to Wrocław**

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# PLENARY LECTURES

## Spectral intensities in cubic systems.

### I.- The $\text{Cs}_2\text{NaEuCl}_6$ elpasolite system

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The optical properties of the  $\text{Cs}_2\text{NaEuCl}_6$  system are reinvestigated on the basis of new and updated experimental data from Raman, electronic, infrared absorption and visible luminescence. These experimental studies have enabled scientists to identify and assign all of the energy levels and corresponding electronic transitions up to  $21,500 \text{ cm}^{-1}$ . Additionally, the crystal field energy levels identification from absorption spectroscopy has been confirmed from additional emission and electronic Raman studies. In this current research work, we decided to investigate the most likely intensity sources, based upon this new set of experimental data and a modified version of the VCF-LP model. Both, the total and relative oscillator strengths corresponding to excitations vibronically allowed are discussed on the basis of a generalised vibronic model. The advantages and disadvantages of our physical models and calculation methods are compared with those of other authors and a full discussion is given in this paper.

### II. – The $\text{Cs}_2\text{NaSmCl}_6$ elpasolite system

On the basis of new and updated experimental information concerning the 10 K luminescence spectrum of  $\text{Cs}_2\text{NaSmCl}_6$ , the 30 K spectrum of the doped  $\text{Cs}_2\text{NaYCl}_6:\text{SmCl}_6^{3-}$  and crystallographic data, we have performed a VCL-LP generalised vibronic intensity calculations for the emissions:  $|({}^4G_{5/2})\Gamma_8\rangle \rightarrow |({}^6H_{9/2})\Gamma_k\rangle, |({}^6H_{7/2})\Gamma_l\rangle, |({}^6H_{5/2})\Gamma_m\rangle$ ;  $\Gamma_k = \Gamma_6 + 2\Gamma_8, \Gamma_l = \Gamma_6 + \Gamma_7 + \Gamma_8$  and  $\Gamma_m = \Gamma_7 + \Gamma_8$ . The calculation is carried out assuming perfect octahedral sites of symmetries for the trivalent  $\text{Sm}^{3+}$  ions, though we are fully aware that below 100K the system undergoes a descent of symmetry from the  $O_h$  to the  $C_{4h}$  point molecular groups, and the degeneracy of the degenerate energy levels being lifted. Both, the calculated overall oscillator strengths and the relative vibronic intensity distributions are reproduced nicely by this model calculations. The most likely sources for improvements are discussed in the text.

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## Optical spectroscopy of nanocrystalline $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ prepared by different synthesis techniques

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In recent years, numerous investigations have dealt with the optical spectroscopy of doped nanocrystals. The interest in this field stems from the observation that the quantum efficiency of the luminescence of these materials increases as the size of the crystals decreases. The search for new and improved phosphors has led to the study of lanthanide doped nanocrystalline inorganic materials as it has been shown that a reduction of the particle size in these crystalline systems leads to modifications of some of their bulk properties. Lanthanide doped  $\text{Y}_2\text{O}_3$  is a well-known oxide phosphor material, which shows improved quantum efficiency when prepared in the nanocrystalline form.

Nanocrystalline cubic  $\text{Y}_2\text{O}_3$  samples doped with 1 and 10 mol%  $\text{Er}_2\text{O}_3$  were prepared utilizing two different synthesis routes. The wet synthesis procedure involved the reaction of an alcoholic solution containing  $\text{Y}(\text{NO}_3)_3$  and  $\text{Er}(\text{NO}_3)_3$  with a basic solution of a surface modifier at  $\text{pH} > 10$ . The combustion synthesis reaction involved an aqueous solution containing glycine,  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The glycine serves as fuel for the combustion reaction, being oxidized by the nitrate ions. For comparative purposes, bulk samples were prepared by intimately mixing the oxides,  $\text{Y}_2\text{O}_3$  and  $\text{Er}_2\text{O}_3$ , pressing the powders into pellets and firing them in air at  $1500^\circ\text{C}$  for 48 hours.

Continuous wave excitation (488 nm) of the bulk and nanocrystalline samples produced strong emission centered at 550 nm, which can be attributed to the transition from the thermalized ( $^2\text{H}_{11/2}$ ,  $^4\text{S}_{3/2}$ ) states to the  $^4\text{I}_{15/2}$  ground state. Emission centered around 675 nm is attributed to the transition from the  $^4\text{F}_{9/2}$  state to the ground state. Excitation of the bulk and nanocrystalline samples at 650 and 815 nm gives rise to upconverted emission. Possible mechanisms leading to the population and relaxation of several excited states are proposed and discussed.

## Search of optimized trivalent ytterbium doped-inorganic crystals for laser applications

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The development of reliable InGaAs laser diode pump sources emitting in the 900–980 nm spectral range is strongly influencing the field of lasers based on  $\text{Yb}^{3+}$ -doped solid state crystals which are searched for new sources from CW to femtosecond regimes. The  $\text{Yb}^{3+}$  ion shows some advantages over the  $\text{Nd}^{3+}$  ion as laser emitting center due to its very simple energy level scheme, constituted of only two levels: the  $^2\text{F}_{7/2}$  ground state and the  $^2\text{F}_{5/2}$  excited state. There is no excited state absorption reducing the effective laser cross-section, no up-conversion, no concentration quenching and no absorption in the green which is favourable in the case of a self-frequency doubling laser.

The first part of this presentation will be focused on the spectroscopic properties of several  $\text{Yb}^{3+}$ -doped crystals useful for laser action. C-FAP ( $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ) and S-FAP ( $\text{Sr}_5(\text{PO}_4)_3\text{F}$ ) of apatite structure which appear to be exceptionally good are grown by the Czochralski technique (CZ) [1–2]. Other  $\text{Yb}^{3+}$ -doped laser crystals have been grown by the following various methods:

- $\text{Y}_2\text{O}_3$  yttria,  $\text{Sc}_2\text{O}_3$  scandia,  $\text{Lu}_2\text{O}_3$  lutecia sesquioxides grown by the Laser Heated Pedestal Growth (LHPG) method [3],
- $\text{LiNbO}_3$  (LNB) lithium niobate [4] and  $\text{Y}_3\text{Al}_5\text{O}_{12}$  yttrium aluminium garnet (YAG), grown by LHPG method,
- oxoapatite  $\text{Ca}_8\text{La}_2(\text{PO}_4)_6\text{O}_2$  (CLYPA) grown by the Micro-Pulling Down Method [5],
- $\text{KY}(\text{WO}_4)_2$  potassium yttrium (KYW) tungstate and  $\text{KGd}(\text{WO}_4)_2$  (KGW) potassium gadolinium tungstate, grown either by the Floating Crystal method [6] and by the Top Seeded Solution Growth (TSSG) [7],
- $\text{CaGd}_4(\text{BO}_3)_3\text{O}$  (GdCOB) and  $\text{CaY}_4(\text{BO}_3)_3\text{O}$  (YCOB) borates grown by the CZ method [8].

The second part of the talk will be devoted with the evaluations based on spectroscopic parameters. The first one [1] only valid for nanosecond pulse extraction modes, is dealing with the emission cross-section  $\sigma_e$  at the laser wavelength and the minimum pump intensity  $I_{\min}$  required to achieve transparency at the laser wavelength. A more recent one [9–11] applied for both CW and amplifier regimes uses the quasi-three level laser dealing with gaussian waves, taking into account, both, the saturation of the pump, the stimulated emission at the pump wavelength, the variation of the laser diode pump, the laser waists and the variation of the laser intensity along propagation. The results of calculations will be visualized in a two-dimensional diagram considering the laser extracted power and the slope efficiency. Tungstates, sesquioxides and YAB have the highest laser potentialities in the CW regime, whereas S-FAP, C-FAP, CLYPA, YAG and tungstates are the most efficient when considering the small-signal gain in amplifier regime.

In addition of these spectroscopic data we shall discuss on the choice of laser crystals by considering comparative values of the thermal conductivities of each type of hosts.

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## **Mn<sup>2+</sup> intra-shell recombination in quantum dots of II-VI compounds**

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Bhargava and Gallagher have proposed [1, 2] that quantum confinement effects in Mn doped quantum dot (QD) structures result in a dramatic reduction of a lifetime of Mn<sup>2+</sup> intra-shell  ${}^4T_1 \rightarrow {}^6A_1$  photoluminescence (PL). The PL decay time of Mn<sup>2+</sup> intra-shell emission is shortened from ms time scale, observed in lightly doped bulk crystals, to ns time scale in Mn doped ZnS QDs. Bhargava [1] suggested that quantum-confinement occurring in QDs enhances s-p hybridization with the d states of Mn ions, which may help to relax spin selection rules for  ${}^4T_1 \rightarrow {}^6A_1$  recombination. The model was then criticized by Bol and Meijerink [3]. These authors related the observed fast component of the PL decay to a decay of another emission band, underlying Mn<sup>2+</sup> PL emission. They concluded that Mn<sup>2+</sup> emission is not affected by doping and confinement conditions. We argue with such explanation of the PL decay data. We present new results of the PL kinetics experiments, which were performed for CdMnTe QD structures and also for bulk ZnMnS samples. For both types of the samples we observed an appearance of a fast component of the PL decay, which is slightly shorter in the case of the above bandgap excitation conditions. Even though we agree with the observation of Bol and Meijerink, that in addition to a fast component of the PL decay a slow one is also observed, we conclude that the shortening of the PL decay time, observed by Bhargava and also by us, is of a different origin than that proposed by Bhargava [1, 2]. This statement is based on the results of optically detected magnetic resonance (ODMR) investigations performed by us on ZnMnS bulk crystals with about 1% Mn fraction. The ODMR experiments indicate efficient relaxation of spin selection rules of Mn<sup>2+</sup> intra-shell PL, which is due to spin cross relaxation effects. We propose that this effect is entirely responsible for a highly efficient Mn<sup>2+</sup> PL observed by us for ZnMnS bulk crystals and for CdMnTe QDs. For close associates of Mn ions spin cross relaxation processes are efficient and the PL decay time is relatively short. If so, a slow decay component of the PL is related to the PL decay of isolated Mn ions, for which spin selection rules affect rate of the Mn<sup>2+</sup> PL recombination.

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## Optical storage and other effects revealed in Si: Er by two-color spectroscopy with a free-electron laser

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Semiconductor matrices doped with Rare Earth (RE) ions feature an attractive combination of sharp atomic like emissions with relatively large cross section of band-to-band absorption. This makes these systems interesting for applications in solid state light-emitting devices. The most investigated systems include InP:Yb, GaAs:Er and Si:Er. The latter one is currently recognized as a successful method for obtaining optical emission from silicon.

Despite numerous studies, the knowledge of excitation and deactivation paths in these complex systems is mostly phenomenological. While the key role of the weakly bound states (excitons, shallow defect states) is generally accepted, details of their particular involvement remain not clear. For the best understood InP:Yb system a detailed energy transfer path has been proposed but urgently requires experimental confirmation. Here we present a spectroscopic approach to this problem by making use of a two-color experimental set-up with a tunable free-electron laser (FEL). Photoluminescence (PL) of RE ions is achieved by primary excitation either with a cw laser diode ( $\lambda_D \approx 720$  nm) or with the second harmonics of a Nd:YAG ( $\lambda_{YAG} = 532$  nm) pulsed laser correlated with the FEL IR pulse. Intense mid-infrared (IR) radiation from the FEL is used to access directly individual steps of the energy transfer processes. Individual shallow levels available in the material are selectively addressed by appropriate tuning of the FEL energy.

In the contribution we will present a variety of effects revealed in Er-doped silicon by two-color optical spectroscopy with the FEL. These include energy storage, excitation transfer between different RE-related optically active centers, and the *so-called* energy “back transfer” effect reversing the 4f-RE core excitation mechanism.



## Inhomogeneous broadening of the $\text{Cr}^{3+}$ sites in $\text{LiTaO}_3$ congruent crystal

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When doped with  $\text{Cr}^{3+}$ ,  $\text{LiTaO}_3$  exhibits strong, broad band emission in the near-infrared resulting from the  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transition. We have shown that the application of high pressure induces a  ${}^4\text{T}_2$ - ${}^2\text{E}$  excited state electronic crossover in  $\text{Cr}^{3+}:\text{LiTaO}_3$ . As a result of the crossover, the broad emission band is replaced by the relatively sharp, structured R lines associated with  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  emission. A detailed analysis of the R lines structure allowed us to distinguish three dominant  $\text{Cr}^{3+}$  sites ( $\alpha$ ,  $\beta$  and  $\gamma$ , all due to  $\text{Cr}^{3+}$  occupying  $\text{Li}^+$  positions) and to characterize the disorder induced distribution of crystal field strength at each site. We have developed a quantitative single configurational coordinate model of the energy and lineshape of  $\text{Cr}^{3+}$  emission over a wide range of pressure. The model included the effects of electron-lattice and spin-orbit coupling. For detailed analysis of the inhomogeneous broadening of the system we have considered temperature and pressure dependence of R lines luminescence kinetics. The luminescence decays have been measured at 63, 83 and 93 kbar between 20 K and 293 K. Similar to ambient pressure behavior the emission decay at each pressure at 20 K was nearly single exponential in character. An increase in lifetime with pressure at 20 K (up to 0.77 ms for 90 kbar) was observed and attributed to a pressure induced decrease of  ${}^4\text{T}_2$ - ${}^2\text{E}$  excited state mixing due to the much higher sensitivity of the energy of the  ${}^4\text{T}_2$  state to pressure. Upon increasing temperature, the emission decay became faster and noticeably non-exponential in character. We attribute the non-exponentiality to the thermal population of an inhomogeneously distributed  ${}^4\text{T}_2$  state arising from disorder in the crystal lattice. Using the energetic structure of the system and crystal field distribution obtained from the luminescence lineshape consideration we have calculated a distribution of the luminescence lifetimes. Good agreement with the resulting experimental lifetime distribution has been obtained. We have found two nonradiative processes that start to be active at high pressure and temperature: the internal conversion processes and non-radiative energy transfer of Förster-Dexter type.

## The rare-earth centers in CsCdBr<sub>3</sub>

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CsCdBr<sub>3</sub> crystallizes in the quasi-linear CsNiCl<sub>3</sub> structure. It possesses linear chains of [CdBr<sub>6</sub>]<sup>4-</sup> octahedra separated by parallel chains of Cs<sup>+</sup> ions. Trivalent Rare-Earth (RE) ions substitute for the divalent Cd ions. The need for charge compensation leads to a number of RE centers, the most prominent of which is the symmetric pair center RE<sup>3+</sup>-(Cd-Vacancy)-RE<sup>3+</sup>. Madelung calculations were performed for a number of different centers giving a ranking for their chance of realization. Experimental evidences are given for the most likely centers by optical spectroscopy and submillimeter EPR. The symmetric pair center is of special interest for cooperative phenomena of RE<sup>3+</sup> ions. This includes direct ion-ion interactions and interactions with or via the electronic excitations of the host lattice. Some relating experiments will be discussed.

## Role of defect states in persistent luminescence materials

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The long afterglow exhibited by some luminescent materials is usually considered as a disadvantageous feature among the properties of the phosphor when the practical applications are considered [1, 2]. Despite the initially unwanted nature of the strong afterglow, there has been a constantly growing market for persistent luminescence materials for several tens of years. The material used so far, ZnS doped with copper is, however, extremely sensitive to moisture and thus chemically unstable. Moreover, the duration of the afterglow is unsatisfactory being of the order of a few hours only.

Since the mid 1990's a completely new generation of persistent luminescence materials has been developed and partly entered into the commercial market, too. These new phosphors originally included only the  $\text{Eu}^{2+}$  doped alkaline earth aluminates,  $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$  ( $\text{M} = \text{Ca}$  and  $\text{Sr}$ ) [3], but other, more complex aluminates as well as other materials are under development. All these phosphors show strong broad band emission characteristic to the  $\text{Eu}^{2+}$  ion in the blue/green visible range. The luminescence lifetime of these phosphors is very long in contrast to ordinary  $\text{Eu}^{2+}$  doped materials, which yield lifetimes of the order of a few tens of nanoseconds.

The overall mechanism of the persistent luminescence is now quite well agreed on to involve the formation of traps followed by a subsequent thermal bleaching of the traps and emission from the  $\text{Eu}^{2+}$  sites. As for the detailed mechanisms involved, no general agreement has been achieved and several interesting and even exciting mechanisms have been proposed. Especially, the mechanisms resulting in the prolonged and enhanced afterglow when  $\text{RE}^{3+}$  ions as  $\text{Dy}^{3+}$  and  $\text{Nd}^{3+}$  are introduced into  $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$  as co-dopants, are completely ignored [4]. In this report, after presenting an initial review on the status on the field, the factors affecting the luminescence properties of these phosphors are described in detail. Finally, the possible mechanisms based on the different defect centers and interactions between them are discussed taking into account the systematic investigations carried out on the preparation, composition, structure and luminescence properties of the  $\text{Eu}^{2+}$  doped alkaline earth aluminates.

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**Stimulated Raman spectroscopy of k(3)-active  $\text{Ln}^{3+}$ -doped laser crystals**

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## Excited state spectroscopy of chromium ions in various valence states in glasses

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Spectral properties of different types of chromium-activated glasses are shown, discussed and interpreted. Chromium in four valence states:  $\text{Cr}^{3+}$ ,  $\text{Cr}^{4+}$ ,  $\text{Cr}^{5+}$  and  $\text{Cr}^{6+}$  is seen in the spectral characteristics of these glasses where  $\text{Cr}^{3+}$ ,  $\text{Cr}^{5+}$  and  $\text{Cr}^{6+}$  play an important role. Trivalent chromium in octahedral coordination reveals the spectra and decays typical for low-field materials with a substantial participation of the site-to-site disorder. Characteristics of the  $\text{Cr}^{5+}$  and  $\text{Cr}^{6+}$  ions appeared to be more interesting. Absorption, excitation and luminescence of the pentavalent chromium ( $d^1$  system) in the octahedral coordination are severely affected by the Jahn-Teller effect, along with the nuances associated with that effect. The hexavalent chromium ( $d^0$  system) in the four-fold coordination, forming the  $[\text{CrO}_4]^{2-}$  group, is seen mostly in the excited state absorption (ESA) spectra that can be interpreted in terms of the transitions between crystal field split terms of the  $\text{Cr}^{5+}\text{O}^-$  centre, which forms after the charge transfer (CT) transition, and between one of those terms and another double-electron state of larger electron lattice coupling, which forms after two consecutive transitions of electrons via the CT transition.

## High energy luminescence excitation of rare earth doped compounds

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Progress in the development of new luminescent materials is directly related to our understanding of physical processes of energy relaxation in solids. One of the most important characteristics of luminescence materials is their efficiency for excitation energy conversion into a fluorescence photon. The total phosphor efficiency depends on the efficiency of the secondary electronic excitation transfer mechanism from the crystalline host to the luminescence center (impurity ion with nearby crystalline environment) and on the efficiency of the radiative relaxation of this center. Determination of the dominant transfer and energy loss mechanisms can be performed by time resolved luminescence spectroscopy using UV-VUV synchrotron radiation (SR) excitation. We will report, the result of studies of a large number of rare earth doped materials, performed in the frame of programmes for search of new efficient VUV phosphors. The experiments were achieved using VUV SR from SuperACO and DCI storage rings at LURE.

Luminescence excitation spectrum below the fundamental absorption edge, or forbidden energy gap ( $E_g$ ) of a matrix, characterizes the efficiency of radiative processes in the luminescence center itself. They are commonly explained on the basis of the simple configurational coordinate model involving Stokes shifts and phonon participation. Below the energy gap, the main direct excitation mechanisms of the luminescence center are :

- (i) electron promotion between the impurity ion quasi atomic states perturbed by the crystal field interaction, especially the so-called f-d transitions,
- (ii) electron transfer from valence band states to excited states of the luminescence center involving molecular orbitals,
- (iii) autoionisation, due to an electron transfer to bound exciton states.

Excitation by photon with an energy greater than  $E_g$  results in the creation of a hot hole in the valence band and of a hot electron in the conduction band. Their relaxation, involving electron-electron inelastic scattering, has a characteristic time of  $10^{-15}$  s and results in the creation of various secondary excitations. During the next stage of the energy relaxation, electrons and holes thermalise with a characteristic time of the order of  $10^{-12}$  s and an energy of the order of 0.5 to  $2E_g$  per electron is used by phonons. Two main excitation mechanisms induced by thermalised electronic excitations are then possible: radiative or non-radiative energy transfer from excitons and sequential hole and electron captures involving a charge transfer. These three excitation mechanisms lead to differences in the luminescence excitation spectra and luminescence decay curves. The same impurity ion can undergo different mechanisms depending on the electronic structure of the host crystal, the space distribution of secondary electronic excitations and the presence of additional electron and hole traps. For example, in fluorides, the capture of  $2p(F^-)$  hole by cerium has a negligible probability since  $4f(Ce^{3+})$  level is situated at rather high energy relatively to the top of the valence band. The fluorescence excitation in these systems is mainly due to the impact mechanism. On the contrary, the high efficiency of cerium doped oxides in general is connected with the close energy location of the  $4f(Ce^{3+})$  level related to the top of the valence band of the crystal, making the capture of the valence band hole by the luminescent centre much easier. Therefore the excitation of cerium by charge transfer mechanism is dominant in oxides.

## Spectroscopy and laser characteristics of $\text{Cr}^{2+}$ -doped chalcogenide crystals. Overview and recent results

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$\text{Cr}^{2+}$ -doped chalcogenide crystals are efficient and broad band tunable solid state laser materials in the infrared spectral range between 2  $\mu\text{m}$  and 3  $\mu\text{m}$ , see Table 1. Pulsed, continuous wave, gain-switched, mode-locked and diode pumped laser operation have been demonstrated in the last years. Possible applications of these mid-infrared lasers include scientific research, remote sensing, trace gas analysis, medicine, and materials processing. In this presentation an overview about the material properties and the laser characteristics of these newly developed laser materials will be given, including the newest results.

Table 1:  $\text{Cr}^{2+}$ -laser materials

Host crystal	Laser wavelength	Slope efficiency	Tuning range
ZnSe [1 - 4]	2350 - 2600nm	73%	2138-2780nm
ZnS [1]	2350nm	30%	
CdSe [5]	2600nm	50%	2560-2730nm
$\text{Cd}_{0.85}\text{Mn}_{0.15}\text{Te}$ [6]	2515 - 2660nm	44%	2300-2600nm
$\text{Cd}_{0.55}\text{Mn}_{0.45}\text{Te}$ [7]	2550nm	64%	2170-3010nm

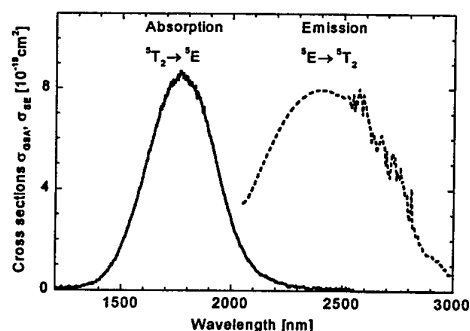


Figure 1: Absorption ( $\sigma_{\text{GSA}}$ ) and emission ( $\sigma_{\text{SE}}$ ) spectra of  $\text{Cr}^{2+}:\text{ZnSe}$  (300K)

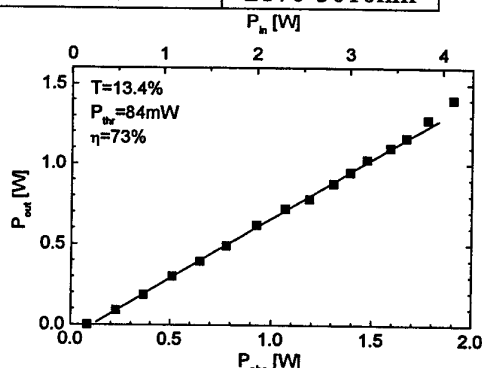


Figure 2: Input-output diagram of the continuous wave  $\text{Cr}^{2+}:\text{ZnSe}$ -laser pumped by a Tm:YAG-laser.  $\lambda_{\text{exc}}=2013\text{nm}$ ,  $\lambda_{\text{em}}=2500\text{nm}$

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## Spectroscopy of nanometer – range media and mixed lanthanide $\text{Ln}\beta_3\text{L}$ compounds. Their application perspectives

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To obtain cathode-ray pumped powder lasers for high resolution monochromatic displays, important is to produce low density scattering media for optically pumped lasers with sufficiently low generation threshold and relatively small volume of the excited medium involved in generation of light. The aim of this presentation is focused on the physical properties and the methods of synthesis of nanosized systems incorporated in silica gel and glasses [1]. Comparison of spectroscopic properties and types of species created in gels and silica glasses will be presented and discussed.

On the other hand, the basically similar compounds to those used as a precursor in creation of nanometer systems can be used in organic layered electroluminescent diodes ( OLEDs). The important characteristics of these materials can be correlated with donor-acceptor properties of the substituents in the ligands.

Moreover, these donor-acceptor properties are responsible for location of energy levels, efficiency of energy transfer, electron-phonon coupling and finally quantum yield of luminescence.

Two types of lanthanide mixed  $\beta$ -diketones will be characterized and their applicability in OLEDs basing on spectroscopic data will be analyzed [2, 3].

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## Luminescence spectroscopy of lanthanide(III) ions in solution

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Luminescence spectroscopy of several Ln(III) characterized by very narrow emission bands and a long decay time is an important technique for the study of coordination chemistry of the lanthanides. Factors affecting the Ln(III) luminescence in solution, that can both quench or increase the intensity and lifetime of luminescence are discussed. The quenching process of the Ln(III) excited states, strongly depended on energy of vibrators resulting from ligands (and/or solvents) and energy gaps,  $\Delta E$ , between the emissive state and the highest sublevel of the ground state of Ln(III), is described. The luminescence lifetime of Ln(III) excited states in aqueous solutions ( $H_2O$  and  $D_2O$ ) are linearly proportional to the number of water molecules in the inner coordination sphere the ion. The correlation has been used to determine the hydration number of Ln(III) ions.

The dominant mode of luminescence quenching of the excited ions, occurring via coupling of the Ln(III) excited state to O–H (and N–H) oscillators from ligand or solvent molecules coordinated to the metal ion, is described. Effectiveness of luminescence quenching by O–H, N–H and other oscillators is discussed. A strong deactivating power of the azide ion,  $N_3^-$ , that effectively quenches the luminescent excited state of the Ln(III) ion in aqueous and non-aqueous solvents, is shown.

The factors, which markedly increase luminescence, efficiently reducing nonradiative energy degradation of Ln(III) ions, are presented. Highly luminescent Ln(III) systems based on complex and ternary complex formation with several groups of ligands (e.g. cryptands,  $\beta$ -diketones, macrocyclic and heterobiaryl ligands, etc.) as well as energy transfer processes are described.

Of particular interest and importance is the use of luminescence selective excitation spectroscopy of the  $^5D_0 \rightarrow ^7F_0$  transition of Eu(III) in the range of 578–581 nm. In this paper recent developments in the use of the excitation spectroscopy of the  $^5D_0 \rightarrow ^7F_0$  transition of Eu(III) and a wealth of information, which can be obtained from this method, are presented. The use of this luminescence technique as a unique and sensitive way to monitor speciation of Eu(III), binding sites in various ligands, to characterize the number of species present in solution and complex stoichiometries are briefly reviewed. A quantitative correlation between the frequency,  $\nu$ , of the  $^5D_0 \rightarrow ^7F_0$  transition of Eu(III) and the coordination around the Eu(III) ion (total formal ligand charge, coordination number), expressed in developed empirical relations reported in the literature are also presented.

## Upconversion processes in holmium activated laser crystals

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In this work we present a review of upconversion processes in several oxide and fluoride materials activated with  $\text{Ho}^{3+}$  ions. The recent interest in these processes is motivated by their use in several classes of new optical devices such as; temperature sensors, IR quantum counter detectors, three different colour emitting phosphors, compact visible or UV solid state lasers. Trivalent holmium ion has several energy levels in the energy range from the near IR to near UV spectral region so many emission and absorption transitions are possible and several mechanisms of upconversion exist. The systems investigated were  $\text{Ho}^{3+}$  doped at various levels; oxide crystals – YAP (Yttrium Aluminum Perovskite –  $\text{YAlO}_3$ ), YAG (Yttrium Aluminum Garnet –  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), planar epitaxial waveguides made of  $\text{Ho}^{3+}$ :YAG on YAG substrates,  $\text{SrLaGa}_3\text{O}_7$  and  $\text{SrLaGaO}_4$ , and fluoride materials – YLF (Yttrium Lithium Fluoride –  $\text{LiYF}_4$ ) crystals and also ZBLAN ( $\text{ZrF}_4+\text{BaF}_2+\text{LaF}_3+\text{AlF}_3+\text{NaF}$ ) glass in a bulk and optical fiber geometry. First we characterize the near UV and visible emissions of  $\text{Ho}^{3+}$  in the investigated systems after selective one photon pumping of the  $^3\text{D}_3$  and  $^5\text{S}_2$  manifold. The fluorescence decays of  $\text{Ho}^{3+}$  ions after pulsed excitation were measured as a function of temperature and holmium concentration. Then these short wavelength emissions were investigated after cw and pulsed IR, red, orange and two colour red plus green upconversion excitations. In the case of cw orange pumping around 590 nm it was found that in YAG, YAP, YLF and ZBLAN an avalanche process is responsible for the upconversion.. The mechanisms and the spectroscopic parameters describing the observed processes have been determined and discussed.

**Overlap polarizability of a chemical bond.  
A scale of covalency and application to lanthanide compounds**

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In this lecture we will firstly introduce the concept of overlap polarizability(OP) of a single chemical bond, and by using certain approximations we will propose an expression for this quantity which depends on the overlap between valence orbitals of atomic species, say A and B, their equilibrium interatomic distance and the energy difference between the HOMO and LUMO of the molecular species AB. An interesting and useful relation involving the bond force constant appears when the CBP is connected with the overlap charge. This concept will be initially applied to the well known hydrogen halides and with this procedure reasonable values of force constants are obtained. On these grounds we will propose a relative scale of covalency. Finally an application to the case of the rather ionic lanthanide compounds, with emphasis to coordination compounds, will be presented and discussed. In this case the SMLC/AM1(sparkle model for lanthanide complexes based on the Austin model 1)[1] is used to obtain the electronic structure and molecular parameters of the compounds. Several relevant aspects of ligand field effects can in this way be rationalized, including the so-called nephelauxetic effect. A relation with previous works on this latter subject will be discussed.

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## Nano sense and nonsense

A. Meijerink

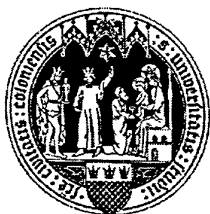
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The electronic structure of nanocrystalline semiconductor particles changes as a function of the particle size. The increase in bandgap and the appearance of discrete energy levels at the band edges as the particles become smaller are known as quantum size effects and have been well studied in the past twenty years, especially for the direct bandgap II-VI semiconductors. Also changes in the luminescence of doped nanocrystalline semiconductor particles have been reported and receive considerable attention in the literature. Unfortunately, next to very interesting articles an impressive amount of nonsense is published as well, also in journals with a good reputation.

This presentation will start with an introduction to quantum size effects. Synthesis methods for doped and undoped nanocrystalline semiconductors will be covered (for example the technique of size selective photoetching). After this, various aspects of the luminescence properties will be discussed. Lifetime measurements for the  $\text{Mn}^{2+}$  emission in nanocrystalline  $\text{ZnS:Mn}^{2+}$  are among the topics where strange results have been published. The radiative decay of the spin-forbidden  $\text{Mn}^{2+}$  emission has been reported to be about  $10^6$  times faster in nanocrystalline  $\text{ZnS:Mn}$  than in bulk  $\text{ZnS:Mn}$  (ns instead of ms). For the same nanocrystalline  $\text{ZnS:Mn}$  particles the non-radiative relaxation has been reported to be  $10^6$  slower than in the bulk ( $\mu\text{s}$  instead of ps). I will try to explain what makes sense and what is nonsense.

A second topic where to my opinion some nonsense has been published concerns the influence of the particle size on the quantum efficiency. For applications a high quantum efficiency is desired and indeed nanocrystalline semiconductors can have a very high quantum efficiency, but the reason is not related to quantum size effects. The high quantum efficiency makes it possible to measure the luminescence of single nanoparticles and some recent results on quantum sized CdSe particles covered with ZnS will be discussed.

Finally, it will be shown how quantum size effects can be used to obtain information that is not easily obtained with other methods. New insight in the luminescence mechanism of the well-known green phosphor ZnO has been obtained by measuring the luminescence properties of ZnO particles of various sizes in the quantum size regime.



## Rare earth halides with exciting oxidation states

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The rare-earth elements belong formally to group 3 of the periodic table, hence have electronic configurations of  $(n)s^2(n-1)d^1(n-2)f^{0-14}$  and, therefore, all of them show oxidation state +3 in compounds. With rare-earth halides, there is one exception:  $\text{EuI}_3$  does not exist. The oxidation state +2 is the highest possible in the presence of the reducing iodide ion.

The oxidation state +2 is also classic. Halides with divalent samarium, europium, and ytterbium are known since the beginning of the 20<sup>th</sup> century. Divalent thulium, neodymium, and dysprosium have emerged intensive research during the last fifty years. In these compounds for which  $\text{TmI}_2$  may serve as an example, the electronic configuration is such that the valence electrons occupy only 4f states, i.e.,  $\text{Tm}^{2+}$ :  $(\text{Xe})6s^05d^04f^{13}$ . These dihalides,  $\text{MX}_2$ , are salts and may be formulated as  $(\text{M}^{2+})(\text{X}^-)_2$ .

There are also diiodides that have semimetallic or even metallic properties. These are typical for the elements lanthanum, cerium, praseodymium, and gadolinium and, at high pressures, also for neodymium. The electronic configuration of „ $\text{Pr}^{2+}$ “ in  $\text{PrI}_2$  is  $(\text{Xe})6s^05d^14f^2$ , and one could also formulate  $(\text{Pr}^{3+})(\text{I})_2(\text{e}^-)$ . The excess electron may be delocalized into a 5d band. It may also give rise to covalent bonding as in  $\text{Pr}_2\text{Br}_5 \equiv (\text{Pr}^{3+})_2(\text{Br}^-)_5(\text{e}^-)$  where triangles of praseodymium atoms are held together presumably by a three-center-one-electron bond. These seem also to be present in the spectacular modification V of  $\text{PrI}_2$  where tetrahedra of praseodymium atoms are the most important structural feature.

Most of the so-called reduced rare-earth halides contain electron donating interstitial elements, mostly light elements like hydrogen and carbon as in  $\text{GdClH}_{0.6}$  and  $\text{Lu}_2\text{Cl}_2\text{C}$ , also nitrogen and oxygen as in  $\text{Pr}_2\text{Cl}_3\text{N}$  and  $\text{Er}_{14}\text{C}_4\text{O}_2\text{I}_{24}$ , but silicon is also possible as in  $\text{Ce}_3\text{Cl}_3\text{Si}$ , and many others. In all of these compounds, single atoms occupy the centers of tetrahedra or octahedra of rare-earth atoms, they form interstitially stabilized clusters. Dicarbon dumbbells also appear as in  $\text{Pr}_5(\text{C}_2)\text{Br}_9$  and seemed to be an exception; with BN and other small groups acting as interstitials this is no longer the case. Bonding in these compounds arises essentially through strong metal-interstitial interaction, metal-metal bonding plays only a minor role.

There are, of course, many open questions. These address, for example, the „non-existence“ of  $\text{LuI}_2$  or the singularity of  $\text{Ho}_5\text{Cl}_{11}$ , or the electronic structure and physical properties of  $\text{LaI}$ . In general, one observes when it comes to reduced halides a pronounced difference between the first half (the first seven, Ce through Gd) and the second half (Tb through Lu) of the lanthanoid elements. We seem to know more about the first than the second half!

## Decorrelation of luminescence signals in fractional energy-transfer upconversion

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Fundamentally important information is contained in the dependence of upconversion-luminescence intensities on pump power. The intensity of an upconversion luminescence that is excited by the sequential absorption of  $n$  photons has a dependence on absorbed pump power  $P$  which may range from the limit of  $P^n$  down to the limit of  $P^1$  for the upper state and less than  $P^1$  for the intermediate states [1]. The commonly assumed slope of the luminescence of  $P^n$  refers to the case of infinitely small upconversion rates. Higher pump power and, consequently, increasing competition between linear decay and upconversion for the depletion of the intermediate excited states result in a significantly reduced slope. If upconversion dominates over linear decay for the depletion of the intermediate excited states, the slope of the luminescence from the upper state  $n$  is almost linear. The slopes of the luminescences from intermediate excited states are even less than linear. These results allow for the interpretation of the slope of a multiphoton-excited luminescence with respect to the order of the process and its physical origin and strength [1].

Energy-transfer upconversion (ETU) is an interionic upconversion process whose probability depends strongly on the distance between the participating ions. ETU is, therefore, influenced by the host geometry, the dopant concentration, energy migration between the active ions, and the distribution of active ions in the host material, which leads to a variation in the nearest-neighbor distances between the active ions.

After two-step excitation by ground-state absorption and ETU (Fig. 1, left-hand side), the luminescence curves in  $\text{LiYF}_4:\text{Nd}^{3+}$  (Fig. 1, center) show the predicted decrease in pump-power dependence. It also shows a correlation between upconversion and downconversion luminescence intensities: The slope of the former is twice the slope of the latter at all pump powers. This correlation derives directly from a simple rate-equation analysis [1]. In contrast, in  $\text{Cs}_2\text{ZrCl}_6: 3.2\% \text{Re}^{4+}$  the measured slopes of upconversion and downconversion luminescence are not correlated to each other (Fig. 1, right-hand side). At the simplest level, this observation can be interpreted as reflecting a scenario in which only a certain fraction of excited  $\text{Re}^{4+}$  ions participates in ETU. This fraction exhibits a slope of its downconversion luminescence which decreases with increasing pump power. In the upconversion luminescence, we only probe this fraction of the excited ions, and observe a slope that also decreases with increasing pump power (similar to the former example of  $\text{LiYF}_4:\text{Nd}^{3+}$ ). The other fraction of excited  $\text{Re}^{4+}$  ions is excluded from ETU. It luminesces from the first excited to the ground state with a linear slope at all powers. The observed downconversion-luminescence intensity is the sum of the contributions from each class of ions. Our model shows agreement with the measured slopes for a fraction of  $40(\pm 10)\%$  of the ions participating in ETU. Although the theoretical method is based on strong simplifications, it illustrates the important principle that upconversion and downconversion measurements need not probe the identical set of dopant ions, and this situation can be identified experimentally.

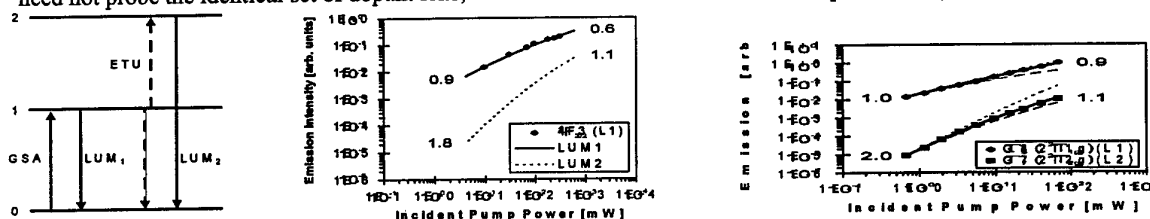


Fig.1. Two-step excitation (left), intensities of downconversion ( $\text{LUM}_1$ ) and upconversion ( $\text{LUM}_2$ ) luminescence versus pump power in  $\text{LiYF}_4:\text{Nd}^{3+}$  [1,2] (center) and  $\text{Cs}_2\text{ZrCl}_6:\text{Re}^{4+}$  [1,3] (right)

The fact that also downconversion and upconversion luminescent transients may probe different classes of ions can be exploited in a simple way to obtain the fraction of ions that fulfill the condition to participate in ETU, independent of the physical nature of this condition. For ions with a qualified energy-level scheme, a simple analytical solution derives [4], which can also be applied to more complex energy-level schemes. This method is independent of the pump and ETU parameters. In principal, it can be applied to investigate the influences of chemical environment and growth conditions on the active-ion distributions in the host material or to probe the influence of energy migration on ETU.

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## Crystal-field levels, hyperfine structure, and relaxation processes in $\text{CsCdBr}_3\text{:Pr}^{3+}$

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This talk summarizes the recent work on  $\text{CsCdBr}_3\text{:Pr}^{3+}$  performed in my group in cooperation with the theoretical group of B. Malkin from Kazan University and two French groups [1, 2]. Crystals of rare-earth (RE) doped quasi-one-dimensional double bromides  $\text{CsCdBr}_3$  are widely studied, mainly, because of their property to incorporate  $\text{RE}^{3+}$  ions in pairs, even at low RE concentrations. This makes them a promising material for up-conversion lasers.

We have performed the low-temperature high-resolution ( $0.05\text{ cm}^{-1}$ ) infrared ( $2000\text{--}7000\text{ cm}^{-1}$ ) absorption measurements of  $\text{CsCdBr}_3\text{:Pr}^{3+}$ . Positions and widths of the crystal field levels within the  $^3\text{H}_5$ ,  $^3\text{H}_4$ ,  $^3\text{F}_2$ , and  $^3\text{F}_3$  multiplets of the  $\text{Pr}^{3+}$  main center have been determined. Hyperfine structure of several spectral lines has been found. We also performed crystal field calculations for the main center in the framework of the semiphenomenological exchange charge model (ECM), based on the analysis of the local lattice structure. Parameters of the ECM were corrected by fitting the calculated hyperfine splittings of crystal field levels to the experimental data from our measurements. The electron-phonon interaction effects, in particular, the low temperature relaxation of excited states of the  $(\text{Pr}^{3+})_2$ -dimer due to one- and two-phonon transitions between the crystal field sublevels of the  $^3\text{H}_5$ ,  $^3\text{H}_6$ ,  $^3\text{F}_2$  and  $^3\text{F}_3$  multiplets, are studied in the framework of the recently derived rigid ion model of lattice dynamics of doped  $\text{CsCdBr}_3\text{:RE}^{3+}$  crystals.

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## Spectroscopic and magnetic observables in 4f-3d mixed compounds: relationship to the structure

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The knowledge of the energy levels plays an important role in the understanding, the simulation and the prevision of the optical and some of magnetic properties of transition and rare earth elements. This is an essential step for the characterization of a crystalline or glassy matrix and its qualification for further applications. The beginning of the talk will present the methods of simulation for the energy level sequence : the different interactions, their relative importance of the phenomenological parameters and the differences between 4f et 3d elements. A special attention will be paid on the determination of the crystal field parameters (cfps) from the crystalline structure by the Simple Overlap Model (SOM) developed by O.L. Malta (1).

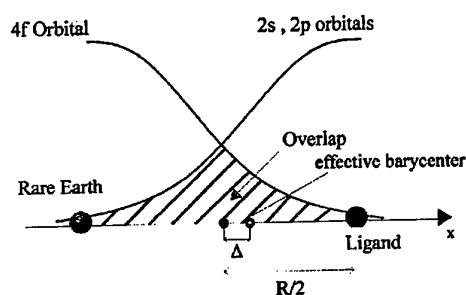


Fig 1 Overlap and effective barycenter as defined in SOM.

The wavefunctions derived from the simulation are used for the calculation of the paramagnetic susceptibility (or the effective moment) by applying the van Vleck formula. This expression includes the thermal population of lowest levels, which is the main responsible for the deviation of the curves from the Curie-Weiss law, observed at low temperature for the rare earth compounds. Usually there is a quite good agreement between the calculated and experimental values as shown on fig. 2.

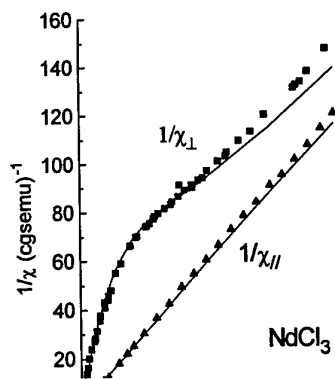


Fig 2. Experimental and calculated variation of the inverse of the paramagnetic susceptibility of NdCl<sub>3</sub> as a function of temperature.

This model has been recently applied successfully to a large variety of solids (2). It considers the overlap  $\rho$  between the 3d or 4f element wavefunctions and those of the ligand  $\mu$ . Its magnitude depends on the covalency of the bonding, also characterized by a small displacement of the charge barycenter. The cfps are calculated from the atomic positions in the first coordination sphere, which permits to make easy calculations in the case of big molecules, as found in coordination chemistry.

$$B_q^k = \langle r^k \rangle \sum_{\mu} \rho_{\mu} \left( \frac{2}{1 \pm \rho_{\mu}} \right)^{k+1} A_q^k(\mu)$$

$$\chi = N\beta^2 \sum_i \left[ \frac{(\epsilon_i^{(1)})^2}{kT} - 2\epsilon_i^{(2)} \right] \frac{\exp\left(-\frac{E_i^{(0)}}{kT}\right)}{\sum_i \exp\left(-\frac{E_i^{(0)}}{kT}\right)}$$

In the case of mixed 4f-3d element compounds an exchange interaction can be found when the temperature goes below the magnetic order transition. This can be experimentally observed by :

- i) the spectroscopic tool with a splitting of the Kramers' doublets in the absorption and emission low temperature spectra
  - ii) neutron diffraction, with peaks appearing down the phase transition temperature
  - iii) a break of continuity in the paramagnetic susceptibility variation vs temperature
- Some examples of such interactions will be shown.

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## Nanosized semiconductor particles in glasses prepared by the sol gel method: their optical properties and potential uses

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Semiconductor nanocrystals (NCs) in transparent media have, especially in sol gel glasses, received recently a large attention due to their promising applications in non-linear optics and optical switches<sup>[1,2,3,4]</sup>. Those nanometer-sized crystals, which are comparable with the bulk exciton Bohr radius, exhibit an intermediate behavior between a bulk crystal and an isolated molecule. For example, CdS and CdSe NCs and CdTe exhibit a large optical non-linearity. Lead sulfide (PbS) is suitable for the telecommunication application, because its bulk band gap is located at 0.41 eV at 300K. The latter is blue shifted to the spectral regime of 0.7–1.5  $\mu\text{m}$  (1.77–0.82 eV) upon the decrease of the PbS NCs diameter below the size of the excitonic Bohr radius (16nm), due to a quantum confinement effect.

The sol-gel process extends the conventional glass melting methods, as it allows incorporation of semiconductor NCs at low temperatures and predetermined concentration and size. Furthermore, the sol-gel technology has advantages in the formation of films with controllable thickness, three-dimensional protection of the NCs, prevention of NCs growth, aggregation and oxidation. In particular  $\text{ZrO}_2$  is an insulating direct wide gap oxide, with an optical band gap of above 5.0 eV, and a refractive index that can be controlled by preparation procedure. Therefore in some cases it has an advantage for preparation of thin films over the more conventional  $\text{SiO}_2$  films prepared by the sol gel process.

We propose to use two methods for the synthesis of CdTe nanoparticles in zirconia sol-gel films. The nanoparticles will be obtained by chemical reduction of Te(IV) using reducing agent (hydrazine) or tin chloride. Particle sizes ranging from 6 to 20 nm in diameter will be prepared by varying the experimental parameters. The size and crystalline structure of the particles will be characterized by optical absorption, X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy. The film morphology will be characterized by scanning force microscopy.

The synthesis will consist of the following steps: preparation of the precursor solution; preparation of the reducing agent or catalyst; mixing of one of them with the precursor solution; film formation; drying and thermal treatment. In order to avert the complete oxidation of the chalcogenide nanoparticles in the sol-gel matrix, the process temperature will be lowered. The same effect will be achieved by the addition of a reducing agent.

PbS nanoparticles will be also prepared in thin films of insulating or conductive glass for optical and/or electrical measurements. The preparation of PbS NCs, embedded in zirconia thin films using of the following steps: preparation of a zirconia solution (1), component solution (2), final solution (3), film deposition, and annealing. The films will be prepared by dipping microscope glass slides or indium-tin oxide (ITO) coated glass substrate into the final solution (3), followed by an annealing process, which completes the chemical reaction between lead and sulfur. The mole concentrations of the PbS NCs within the zirconia films will be 5, 15, 20, and 30%. The thickness of the investigated films will be controlled by the variation of the solutions viscosity. The latter strongly depends on the concentration of zirconia tetrapropoxide in the zirconia solution. The quantum size effect (shifting of the absorption and emission maxima to higher energies of ~0.5 eV) will be compared with the size of nanoparticles obtained from TEM measurements.

For electrical measurements gold electrodes with typical areas of  $3\text{mm}^2$  will be evaporated in vacuum on top of the films. The final sandwich structure, ITO/PbS NCs in  $\text{ZrO}_2/\text{Au}$ , will be obtained by this method. Reference sample of pure  $\text{ZrO}_2$  film, deposited between the ITO and gold contacts, will be prepared. The electrical measurements will allow us together with the optical measurements to construct new optoelectronic devices.

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**Design of highly luminescent lanthanide coordination complexes:  
Synthesis and applications**

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**Relativistic model of energy transfer in rare earth doped materials****L. Smentek<sup>a,b</sup>, B.G. Wybourne<sup>a</sup>, and B.A. Hess Jr.<sup>b</sup>**<sup>a</sup>*Instytut Fizyki, Uniwersytet Mikołaja Kopernika, Toruń, Poland, E-mail: smentek@phys.uni.torun.pl*<sup>b</sup>*Department of Chemistry, Vanderbilt University, Nashville, Tennessee, USA*

The theory of energy transfer in rare earth doped materials is developed in relativistic language that is formulated within the concept of  $L$ - $S$  coupled states. The approach is defined by means of Sandars and Beck's transformation of inter-shell unit tensor operators to their relativistic form expressed by *doubly effective double* tensor operators. The tensorial structure of the new effective operators is analyzed, and new selection rules for the non-vanishing contributions to the energy transfer amplitude are presented.

## Nanometric luminophors based on Eu and Tb doped compounds

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Different preparation methods of nanometric luminophores based on europium and terbium compounds are presented. Their structural and morphological features are reported. The effect of particles size on luminescence behavior was investigated. The dependence of luminescence properties of nanometric luminophores on excitation power was observed.

**Relativistic effects in lanthanides and actinides****Brian G Wybourne and Lidia Smentek***Instytut Fizyki, UMK, ul. Grudziadzka 5/7, 87-100 Torun, Poland, E-mail: bgw@phys.uni.torun.pl*

The Judd-Ofelt theory of  $f \leftrightarrow f$  transitions was originally developed as a non-relativistic theory nearly 40 years ago. Modifications to include the effects of spin-orbit effects have been developed by various researchers. The inclusion of relativistic effects both for the Judd-Ofelt theory of intensities and for crystal field effects has been hindered, until recent times, by the lack of adequate relativistic radial integrals. It is now possible to obtain reliable relativistic integrals and we show how both the Judd-Ofelt theory and crystal field theory may be modified to accommodate relativistic effects. These extensions involve new effective operators. We include some historical remarks on the development of the Judd-Ofelt theory.

## Thermal quenching characteristics of luminescence from RE ions in GaN thin films

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We have studied the thermal quenching characteristics of visible and infrared luminescence of Er-doped GaN and Eu-doped GaN thin films. The GaN: RE samples were grown by solid-state molecular beam epitaxy on Si (111) substrates. Under above-gap pumping, characteristic green (~537nm) and red emission lines (~622nm) were observed from Er<sup>3+</sup> and Eu<sup>3+</sup>, respectively. The GaN:Er samples also exhibited strong emission lines in the infrared (~1535nm) which showed a remarkable temperature stability from 10K to 500K. There was less than a 10% decrease in the integrated PL intensity. However, the integrated PL intensity of green emission from GaN:Er was not nearly as stable. A 40% decrease was observed from 77K to room temperature. The integrated PL intensity of red emission from GaN:Eu decreased even more rapidly (~factor of 20) over the same temperature range. Temperature dependent lifetime measurements suggest that non-radiative decay processes only weakly affect the intra-4 luminescence of both systems at room temperature. A more detailed discussion of the luminescence dynamics, and rare earth concentration dependence will be presented at the conference.

## From molecular engineering to molecular nanoelectronics

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Factors inducing popping up of new branches of science and general rules of euristics will be discussed first. Then the problems of molecular engineering, leading to molecular nanoelectronics, will be contemplated, such as:

1. Little's model of organic high temperature superconductors Bihole.
2. The nature of high values of nonlinear susceptibility of aromatic compounds and experimental demonstration of its dependence on intramolecular charge transfer.
3. LUMO and HOMO and electron and hole conductivity of materials for the thin film Organic Light Emitting Diodes (OLEDs).
4. Molecular layers – “new” solution of general problems of nanoelectronics – high accuracy of manufacturing nanometer-scale periodic structures and charge-carrier mobility in organic materials.
5. Photonic crystals, nanometer-size scale periodic structures, quantum dots, and the problem of synthetic opals. ZnO powder lasers with optical and cathode-ray pumping. Effect of seeds size in fine powder of luminophores. Displays with low persistence.
6. Special tracks of jumping charge-carriers to recombination sites. Trans-membrane charge transfer in biology. Proton conductivity and hydrogen bonds. Intra- and intermolecular charge transfer.
7. Lanthanide probe of cation sites – luminescence of acid lanthanide oxalate, CD of the tetracycline salts. Influence of hydrogen bonds and zwitter-ions.
8. Lanthanide probe of the energy transfer to cations with low redox potential, W. de W. Horrocks system and its model consisted of lanthanide salts of tautomeric pyridine-dicarboxylic acids.

Molecular nanoelectronics studies methods of manufacturing and processes of charge transfer in molecular systems with periodic structures of nanometer-size scale. Electron transfer in such systems can be influenced by hydrogen bonding and zwitter-ions.

The work was supported by the Russian Foundation for Basic Research (grant N 01-02-16837)

# ORAL PRESENTATIONS



## Up-conversion fluorescence dynamics from the dynamically splitted high-lying excited state of cluster centers in the $\text{CaF}_2$ neodymium doped crystal

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Detailed site-selective and time-resolved fluorescence and kinetic laser spectroscopy with high spectral and nanosecond temporal resolution was provided for the M and N absorption bands of the  $^4\text{I}_{9/2}(1) \rightarrow ^4\text{G}_{5/2}(1)$  hyper-sensitive transition in the  $\text{CaF}_2:\text{Nd}^{3+}$  (0.6%) crystal at 4.2K. Nanosecond dynamics of up-conversion fluorescence from the  $^4\text{D}_{3/2}$  excited state in the pair M- and quartet N-centers by the excitation into the  $^4\text{G}_{5/2}(1)$  excited state was investigated. Different types of the dynamically splitted pair M-centers with slightly different positions of spectral lines and lifetimes of the  $^4\text{F}_{3/2}$  and  $^4\text{D}_{3/2}$  excited states disguised by different M'-centers formed by  $\text{Nd}^{3+}$  and unintentionally doped  $\text{Y}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ , etc. were found. Some mechanisms of nanosecond up-conversion are discussed. An attempt was made to find intrinsic optical bistability in the pair M- and quartet N-centers.

This work was partially supported by grants of RFBR 99-02-18212a and RFBR-DFG No 436 RUSS 113/132/0 (a 00-02-04007), INTAS 96-0232, NSF grant ECS-9710428.

**Anti-Stokes luminescence and site selectivity in  $\text{La}_2\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$** **P. Boutinaud, P.T. Diallo and R. Mahiou**

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The luminescence properties of 5 mol%  $\text{Pr}^{3+}$ -doped  $\text{La}_2\text{Ti}_2\text{O}_7$  are investigated at low temperature upon various laser excitations. As the structure of this titanate offers 4 different crystallographic sites for the praseodymium ions, the spectral lines attribution is made a hard task. The spectroscopic study shows that while the attribution of  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  emission lines is not accurate on the basis of Stokes spectra, spectral site selectivity and lines attribution can be achieved successfully by considering orange-to-blue anti-Stokes spectra. A qualitative model is proposed to interpret the up-conversion mechanism in this material.

## Fine-tuning of the chromaticity of the emission colour of organic/inorganic hybrids incorporating $\text{Eu}^{3+}$ , $\text{Tb}^{3+}$ and $\text{Tm}^{3+}$

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Efficient light conversion molecular devices (LCMDs) based on lanthanide complexes may certainly find a series of important applications, such as luminescent labels in fluoroimmunoassays, antennas in photosensitive bioinorganic compounds and high technology optics [1]. The design of lanthanide complexes acting as efficient LCMDs is, thus, an important theme in supramolecular and coordination chemistry, being pursued by several groups [1]. On the other hand, a recent series of organic/inorganic hybrid hosts have been synthesized due to the possibility of tailoring the properties of novel multi-functional advanced materials through the combination at the nanosize level of the organic and inorganic components in a single material [2, 3].

This work presents the synthesis and luminescence properties of organic/inorganic sol-gel derived hybrids incorporating different concentrations of  $\text{Eu}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{Tb}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Tm}(\text{NTA})_3 \cdot 2\text{H}_2\text{O}$  complexes, NTA is naphthyltrifluoroacetone. The hybrid organic/inorganic matrix, termed di-ureasil, is formed by a siliceous backbone covalently bonded to polyether-based segments (average molecular weight of 2000 g/mol) via urea cross-linkages [3].

The emission spectra strongly depend on the temperature and excitation wavelength. At room temperature, RT, and for excitation wavelengths between 340 and 365 nm, the intra- $4f$  lines of the  $\text{Eu}^{3+}$ ,  $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ , and the  $\text{Tb}^{3+}$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_{2-6}$  could be detected. The  $\text{Tm}^{3+}$  emission is only detected at low temperatures. For an excitation wavelength of 395 nm, a large broad band between 400 and 350 nm, ascribed as the hybrids' host emission is also detected. This emission is originated from electron-hole recombinations in the NH groups of the urea linkages and electron-hole recombinations occurring in the siliceous nanodomains. By lowering the temperature the relative intensity between the  $\text{Eu}^{3+}$  and the  $\text{Tb}^{3+}$  lines changes and the emission of the hybrids is dominated by the green color characteristic of  $\text{Tb}^{3+}$  emission. This can be illustrated by calculating the (x,y) CIE, Commission Internationale d'Éclairage, color coordinates that change from the pink region (0.47, 0.32), at RT, to the yellowish-green one (0.32, 0.58) at 14K, for an excitation wavelength of 360 nm.

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## Spectroscopy of 5d-levels of $\text{Ce}^{3+}$ in inorganic compounds

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The location of the lowest energy  $4f^{n-1}5d$  excited state of the trivalent lanthanides, which is of crucial importance for many technological applications, depends both on the type of lanthanide ion and the type of host crystal [1].  $\text{Ce}^{3+}$ , having just one electron in its 4f shell, shows the simplest spectroscopy of all the lanthanides. On excitation to the 5d-configuration there are at most five different final states. These 5d-energy levels are at relatively low energy and can be observed in absorption or luminescence excitation experiments.  $\text{Ce}^{3+}$  is therefore the ideal dopant to study the relation between 5d-level energies and the crystalline environment.

By now properties of  $\text{Ce}^{3+}$  5d-levels are known in about 400 different inorganic compounds comprising the fluorides, chlorides, bromides, iodides, oxides, sulfides, and selenides. For a subset of about 80 of these compounds information is available on all five crystal field split 5d-levels [2, 3]. In this paper we concentrate on the average (centroid) energy and the extent of the 5d-configuration. It appears that the nearest coordination shell of anions around  $\text{Ce}^{3+}$  determines both the centroid energy and the extent, i.e. total crystal field splitting. What is more, crystal field splitting and centroid shift appear to behave independently from one another. This greatly facilitates analysis since both properties can be dealt with separately. Crystal field splitting is determined by the size and shape of the anion polyhedron. Surprisingly, the type of anion, its charge state or its chemical properties, appears

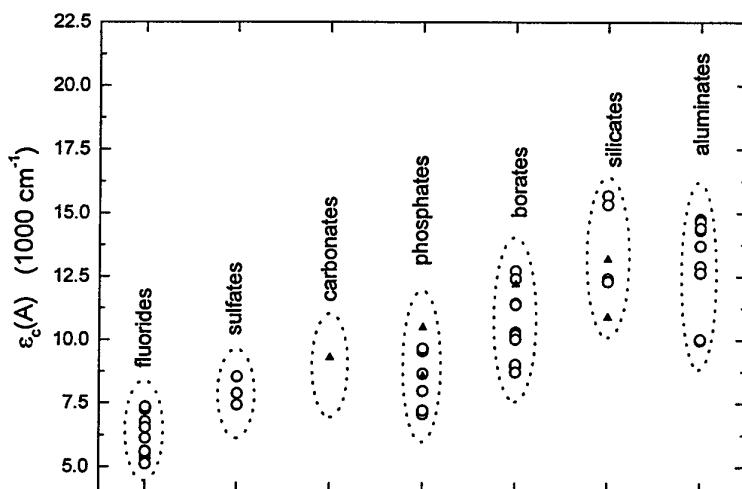


Figure 1. Shift of the 5d-centroid energy of  $\text{Ce}^{3+}$  in inorganic compounds relative to the free ion value ( $51230 \text{ cm}^{-1}$ ).

to be of minor importance. On the other hand centroid shift is strongly determined by the chemical (covalence) and physical (polarizability) properties of the anion ligands, see Fig. 1.

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## Enhanced luminescence of lanthanides from xerogel solids embedded in porous anodic alumina

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Fabrication of silica, titania or alumina xerogel films doped with Er, Tb or Eu onto porous anodic alumina 1-30 microns thick reveals strong enhancement of lanthanides photoluminescence (PL) in comparison with xerogels fabricated onto flat surface of silicon wafers [1-5]. The total integral intensity of lanthanides PL increases with the increase of the porous anodic alumina thickness and number of xerogel layers, mesoscopically confined in porous anodic alumina. For example, terbium luminescence from porous anodic alumina 30 microns thick spin-on coated with Tb-doped xerogel in a single step is 15-20 times greater than that from terbium-implanted thin films. The results are compared with experimental data obtained for erbium and terbium doped microporous silica globules. It was found that exploiting of porous anodic alumina as a template for xerogel host materials reduces significantly the temperature quenching of lanthanides. Possible mechanisms driving the enhancement of lanthanides PL in the structure microporous xerogel/mesoporous anodic alumina are discussed.

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## Spectral and dynamic study of the broad band UV $4f^25d \rightarrow 4f^3$ emission in Nd-doped double sodium yttrium fluoride crystals

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$4f^{n-1}5d \rightarrow 4f^n$  interconfigurational transition studies of rare earth-doped crystals are of importance to several optical domains of application, such as luminescent materials for mercury free fluorescent tubes, plasma display panels, scintillators or tuneable UV solid-state laser materials. In this last research field, to avoid generation of colour centres under high energy VUV excitation, upconversion pumping with less energetic photons is considered.

We present here our recent spectroscopic study of the highly excited states of  $Nd^{3+}$  ions in the double sodium yttrium fluoride  $Na_{0.4}Y_{0.6}F_{2.2}$  (NYF). This crystal has a modified structure of fluorite  $CaF_2$  in which 40% of  $Ca^{2+}$  ions are replaced by  $Na^+$  ions and the remaining 60% are replaced by  $Y^{3+}$  ions. This matrix enables doping with the RE ions in high concentrations, neodymium entering coefficient in NYF: $Nd^{3+}$  crystals is 0,85. The neodymium concentration in the samples was determined by X-ray spectral analysis with the electron-probing micro-analyser Camebax. We studied eight samples with different concentration varying from 0.3 up to 20 at% Nd.

As already observed in other Nd-doped fluoride crystals [1], excitation with the third harmonic (355 nm) of a nanosecond pulsed Nd:YAG laser leads to intense upconversion emission bands between 180 and 320 nm. In NYF:Nd, the three broad bands centred at 190, 235 and 268 nm are assigned to transitions from  $4f^25d$  states to  $^4I_{11/2}$ ,  $^2H_{9/2}$  and  $^2G_{7/2}+^2H_{11/2}$   $4f^3$  levels respectively. A much narrow band located at 217 nm is attributed to the  $^2G(2)_{9/2} \rightarrow ^4I_{11/2}$   $4f^3$  intraconfigurational transition. Its decay time is decreasing from 7 to 0.2  $\mu s$  by increasing the  $Nd^{3+}$  concentration from 0.3 to 20 at%. The  $4f^25d \rightarrow 3f^4$  emission bands are much faster; their decay time, measured after direct excitation in the lowest  $4f^25d$  states with a hydrogen lamp (pulse length 1 ns, repetition rate 10Hz), are of the order of 37 ns whatever the  $Nd^{3+}$  concentration value. A VUV excitation spectrum recorded by selecting the  $4f^25d \rightarrow 3f^4$  emission with a solarblind filter reveals the structure of the lowest interconfigurational  $^4I_{11/2} \rightarrow ^25f_1$  bands: the first one, centred at 175 nm, is the most intense then three other bands are located at 157, 142 and 135 nm. Finally upconversion pumping of the  $4f^25d$  states was also considered using  $^4F_{3/2}$  as the metastable absorbing level, and an excited state absorption cross section of  $1.2 \cdot 10^{-18} \text{ cm}^2$  was measured for the  $^4F_{3/2} \rightarrow 4f^25d$  absorption band located at 190 nm. This cross section value is of the same order of magnitude as those measured in other Nd-doped wide band gap fluoride crystals [2].

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## ***Ab initio* theory of the electronic structure and levels schemes of $nl$ -ions in solids and clusters**

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Our communication is devoted to the consideration of the foundation and results of the self-consistent field theory for  $nd$ - and  $nf$ -ions in  $ME^{+n}[L]_k$ -clusters and solids. We have to consider the electronic structure, energy levels and electronic transitions for the clusters with  $3d$ - and  $4f$ -ions. We analysed theoretical and experimental data for optical and X Ray transitions by used of our approach of consideration for RE and AC ions into  $ME^{+n}[L]_k$ -clusters where  $L=F^-$ ,  $O^{2-}$ . We may conclude that we have got our theoretical data are closely corresponded to experimental data.

We have received the general system of equations of the self-consistent field for cluster in liquids and solid states [1-2] which is quite simple and similar Hartree-Fock-Pauli one. Results of calculations of the energy structure of clusters and values of Slater's (Racah's) radial integrals for Me and RE-ions in 1-23 superconductors and  $nl$ -ions in garnet, perovskite and others crystals are qualitatively and quantitatively correct.

We've got the best results for pressure dependence of Cr and Nd ions spectra in ruby or garnet, change of optical and X-Ray spectra after irradiation of oxide single crystals [8]. We explained the nature of anomalous in  $SrTiO_3$  [9] and separate lasers crystals by used of results of the calculations. In the framework of our approach we obtained the best accuracy for the energy of X Ray lines for all  $nf$ -ions in solids and liquids [10-11].

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## Laser and spectral properties of Yb doped KYW microchip laser

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Ytterbium doped potassium yttrium tungstate ( $\text{KY}(\text{WO}_4)_2\text{:Yb}^{3+}$  or Yb:KYW) is known as an efficient laser medium for miniature diode pumped solid-state lasers, including Raman lasers with self-frequency conversion. In this communication we present the results on investigation of Yb:KYW diode pumped microchip laser CW operation to our knowledge for the first time.

The microchip laser was made of a 1 mm thickness Yb:KYW crystal cut along the b axis and HR/AR coated in the wavelength range 1010–1160 nm on the pump/output facet, respectively. The crystal was mounted with the AR coated surface in close proximity to the flat output coupler

Maximum slope efficiency of about 23% and best efficiency relative to incident pump power of 10% were achieved with an output coupler with 10% transmission (Fig.1).

While decreasing output coupler reflectivity, there is a tendency to red shift of laser wavelength, which can be explained by changes of internal losses of the cavity (Fig. 2).

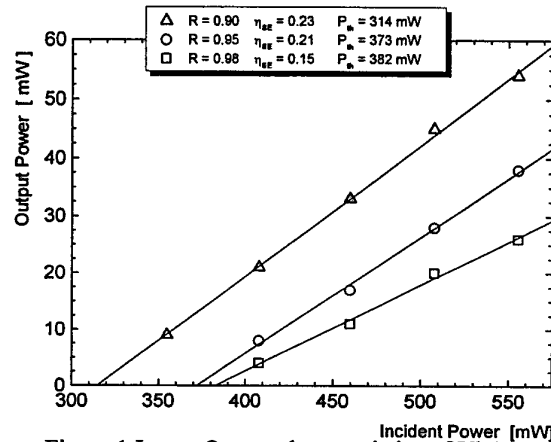


Figure 1 Input-Output characteristics of Yb:KYW microchip laser

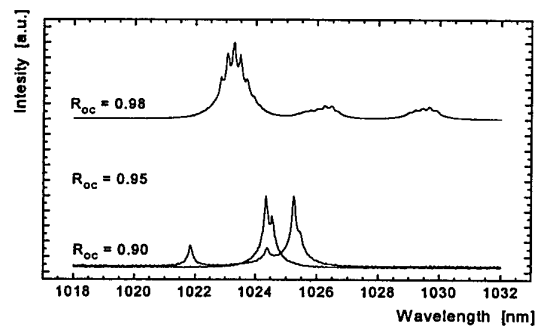


Figure 2 Microchip laser output spectrum



**Growth of rare earth (RE) concentration gradient crystal fibers and  
analyse of dynamical processes of laser resonant transitions  
in RE-doped  $\text{Y}_2\text{O}_3$  (RE=  $\text{Yb}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ho}^{3+}$ )**

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A new and original method has allowed us to grow rare earth concentration gradient crystal fibers by using the LHPG (Laser heated Pedestal Growth) technique [1-3]. Composition of rare earth dopant in these samples varies continuously from one end to the other end of the fiber, between two previously chosen concentrations. We have already used this technique to study spectroscopic properties of doped and codoped refractory optical crystals like  $\text{Y}_2\text{O}_3$  [4-5].

Yttria is an attractive host material for laser applications for several reasons: it is a refractory oxide with a melting point of 2380 °C, a very high thermal conductivity,  $\kappa_{\text{Y}_2\text{O}_3} = 27$  W/mK, two times YAG's one,  $\kappa_{\text{YAG}} = 13$  W/mK. In addition, this crystal has the cubic body centered structure with the space group  $\text{Ia}_3$  ( $T_h^7$ ) and then it is optically isotropic, with a refractive index of 1.91. Another interesting property allowing radiative transitions between electronic levels is that the dominant phonon energy is 380  $\text{cm}^{-1}$  which is one of the smallest phonon cutoff among oxides. It is obvious that the high melting point of this oxide is an obstacle for classical crystal growth techniques yet the growth by the Czochralski method can only be performed in expensive rhenium crucible [6]. We have to mention that the crucible-less LHPG apparatus is then well adapted to elaborate refractory materials under the shape of small crystal fibers.

In this work we are particularly interested in analyzing dynamical processes of resonant transition of three rare earth ions in yttria:

- $\text{Yb}^{3+}$  with the  $^2F_{7/2} \leftrightarrow ^2F_{5/2}$  transition around 1030 nm,
- $\text{Er}^{3+}$  with the  $^4I_{15/2} \leftrightarrow ^4I_{13/2}$  transition around 1540 nm,
- $\text{Ho}^{3+}$  with the  $^5I_7 \leftrightarrow ^5I_8$  transition around 2050 nm.

We shall describe the technique to grow samples with special gradient crystal fibers and we shall also show how to measure absolute concentrations of rare earth ions. Then, we shall analyse the dependence of the concentration on the processes of the involved energy transfer for each type of rare earth ion. Our study will be based on experimental results like the initial rise times and the decays of fluorescence under selective laser pumping.

Our main objective is to point out the interest to grow concentration gradient fibers so as to study excited state dynamics as an original and efficient tool for spectroscopy of inorganic optical materials.

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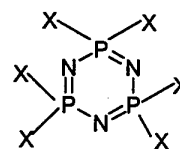
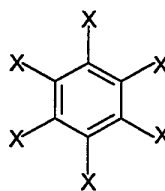
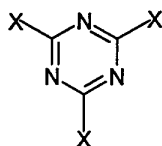
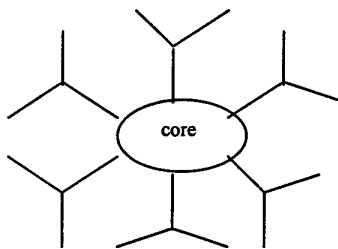
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## Highly luminescent lanthanide complexes based on dendrimeric phosphinoxides

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Dendrimeric molecules possessing O, N, S, P donors are unique complexing agents for all conceivable metal ions, capable of forming polynuclear complexes. Of particular interest is their potential in catalysis, photocatalysis, electroactivity, and more recently in light energy conversion. In particular, it is very interesting to design dendrimeric molecules for lanthanide ion complexation to form multinuclear paramagnetic lanthanide complexes for magnetic resonance imaging, and as luminescent materials. Multibranched dendrimers possessing sensitising units on the periphery of the molecule would be suitable systems for efficient devices based on Absorption-Energy Transfer-Emission process. Schematic representation of branched dendrimer molecule is shown below, together with simple dendrimers of 1st generation, where the core molecule is benzene ring, 1,3,5-triazene, and cyclotriphosphazene possessing phosphinoyl units as lanthanide ion sensitisers.



Schematic representation of dendrimer

X = phosphinoyl group

These small dendrimers turned out to be very good complexers for Eu(III) and Tb(III) ions, and very powerful emission sensitisers. Important point was that very strong red and green luminescence upon UV irradiation at 254 nm was observed in water solution, which makes these systems particularly useful for their potential biomedical applications based on time-resolved fluoroimmunoassays.

Absorbance, excitation and fluorescence spectra, as well as the luminescence lifetimes and quantum yields will be discussed in details.

## Multiphonon sideband intensities in RE ions in crystals

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Multiphonon sidebands play an important role in the dynamic processes of Rare-Earth (RE) doped materials since they rule multiphonon nonradiative processes as well as multiphonon assisted energy transfers. Vibronic sidebands may originate from two main classes of processes which have been usefully separated by Miyakawa under the name of  $\Delta$ - and M-processes. Because RE ions usually have very small Huang-Rhys  $S_0$  parameter ( $10^{-3}$ – $10^{-2}$  to be compared to 100 for F-centers for which such parameter was first defined), the multiphonon sideband case for the M-process can be a useful approach. Here, we will consider multiphonon transitions in the M-process case; vibronics are induced by the joint action of the electromagnetic field and the high-order optical anharmonicity. The processes under consideration give rise to Stokes and anti-Stokes multiphonon sidebands in emission and absorption spectra. Besides, these processes can significantly increase the transition rate in presence of the stimulated emission field existing in an active material above laser threshold. In our calculations, the crystal field model, taking into account both Coulomb and non-Coulomb interactions of 4f-electrons with ligands, is considered. The "electronic part" of the end-result has the same form as the well-known Judd-Ofelt expression for  $J \rightarrow J'$  radiative transition probability. A simplified form of the general expression is proposed.

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## Nonstoichiometric potassium lanthanum double phosphates

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Compounds of the type  $K_3La(PO_4)_2$  have been prepared as earlier described [1-3] by solid state reactions or are drawn from a diphosphate flux as well, using rare earth oxides or precipitated  $LnPO_4 \cdot nH_2O$  (Rhabdophane structure, [4]). The symmetries of the unit cells are monoclinic (SG  $P2_1/m$ ;  $Z=2$ ) and corresponds to  $K_3Nd(PO_4)_2$ , as described by HONG and CHINN [5].

Recently we reported on phonon coupled electronic transitions at 2950 Å in excitation spectra of  $K_3Eu(PO_4)_2$  detected at 5900 Å [6]. It seems necessary to study undoped host compound potassium lanthanum double phosphate of known nonstoichiometry prepared by identical conditions to produce nonstoichiometry defects in this lattice. Some hints in connection with density determinations on little single crystals in Clerici's solution and neutron activation analyses on different single crystals earlier lead to this assumption [2, 7].

Therefore samples were prepared of different cation anion ratio. Besides the stoichiometric mixture of starting materials we tried to prepare samples with an excess or a lack of cations. Preparation using high purity lanthanum compounds was carried out by little modified conditions and this results in powdered materials of the same crystal structure.

At room temperature and the usual UV excitation no emission could be observed. But at low temperature (10 K) and the high excitation intensity of synchrotron radiation used at experimental station SUPERLUMI broad emission bands were observed for the nonstoichiometric materials in contrast to the stoichiometric one. The emission properties confirm that depending on cation anion ratio different kinds of defects are formed and that they are not caused by impurities of the lanthanum. We assume the formation of defects, forming color centers due to trapping of free electrons which are formed by absorption of synchrotron radiation. The situation in these double phosphates may be similar to color center formation in  $KTiOPO_4$  [8].

### Acknowledgements:

The authors acknowledge gratefully the support of Prof. Georg Zimmerer, Dr. Marco Kirm and DP Elke Gminder (Univ. Hamburg, II. Institut für Exp. Physik; HASYLAB im DESY Hamburg) as well as Dr. Harm Wulff and Ing. Brigitte Witt (Univ. Greifswald). The work was funded by the Deutsche Forschungsgemeinschaft (DFG - Contract SCHW 498 / 6-2).

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## Energy transfer between $\text{UO}_2^{2+}$ and $\text{Eu}^{3+}$ in $\text{POCl}_3\text{-SnCl}_4$ solutions

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The solutions of rare-earth elements in complex aprotic solvents  $\text{POCl}_3\text{-SnCl}_4$  are of considerable interest as mediums for lasers and optical quantum amplifiers. In  $\text{POCl}_3\text{-SnCl}_4$  the active ions of rare-earth elements form mononuclear discrete complexes, which poorly interact with each other and with a solvent. Due to this particular feature it is possible to reach a high quantum output of luminescence (more than 90%) and in such solutions a concentration quenching process is practically absent. However, the same feature does not allow to lift pumping efficiency of active ions, in particular  $\text{Eu}^{3+}$ , at the expense of the energy transfer from any other ion-sensitizer. Our recent investigations have shown that under certain conditions in solutions  $\text{POCl}_3\text{-SnCl}_4$  containing rare-earth elements (III) and uranyl (VI) there can arise the polynuclear complexes, inside which a rather effective transfer of the excitation energy is possible [1].

In this report the results of the study of interaction between  $\text{UO}_2^{2+}$  and  $\text{Eu}^{3+}$  in solutions  $\text{POCl}_3\text{-SnCl}_4$  with a constant europium concentration and a variable uranyl concentration are represented. It has been found that the intensity of the over sensing absorption band  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  of an ion  $\text{Eu}^{3+}$  increases in more than 10 times with increasing concentration  $\text{UO}_2^{2+}$ . The change of branching factors for transitions  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (increase) and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$  (reduction) is revealed in the  $\text{Eu}^{3+}$  luminescence spectra. The intense europium luminescence associated with uranyl sensitizing is registered in excitation spectra of ions  $\text{Eu}^{3+}$  in the range of 350-500 nm. The rate constant for the energy transfer from  $\text{UO}_2^{2+}$  to  $\text{Eu}^{3+}$  is derived and its value is determined to be about  $5 \cdot 10^5 \text{ M}^{-1}\text{sec}^{-1}$ . The europium emission and uranyl quenching has provided an evidence for a complex being formed between  $\text{UO}_2^{2+}$  (donor) and  $\text{Eu}^{3+}$  (acceptor). The excitation energy transfer between donor and acceptor is realized within a polynuclear bridging complex of the type  $\text{UO}_2^{2+}\text{-}\mu\text{-Eu}^{3+}$ , in which europium and uranyl are connected among themselves, most probably, dichlorophosphate groups.

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## High-pressure luminescence study of $\text{LiNbO}_3\text{:MgO,Cr}$ and $\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}\text{:Cr,Nd}$ crystals

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The high-pressure low temperature luminescence measurements in diamond anvil cell is a very powerful tool for studying the energy structure of  $\text{Cr}^{3+}$  ions in various compounds. Application of high-pressure reduces the distances between a dopant ion and the ligands. Thus it increases the strength of the crystal field experienced by the dopant centers, allowing to obtain information about their electronic structure. This technique is especially useful for crystals with very low strength of the crystal field experienced by chromium ions at ambient pressure. The first excited state of  $\text{Cr}^{3+}$  in the low strength crystal field octahedral environment is a  ${}^4\text{T}_2$  state. Optical transitions from this state to the ground  ${}^4\text{A}_2$  state are spin-allowed and strongly coupled to the lattice. This results in the broad-band luminescence with relatively short decay times, in contrast to the strong strength crystal field situation, when the first excited state of the  $\text{Cr}^{3+}$  ions is the  ${}^2\text{E}$  level, weakly coupled to the lattice. Optical transitions from this level to the ground state are spin-forbidden. Therefore the luminescence from this state has a form of sharp R-lines with long decay times. Application of pressure transforms the low strength crystal field into high strength crystal field. This way it increases the spectral resolution of measurements. This effect will be shown using three types of the crystals doped with chromium: congruent and near-stoichiometric  $\text{LiNbO}_3$  and lanthanum lutetium gallium garnet (LLGG).

It is shown that in near-stoichiometric  $\text{LiNbO}_3$  crystals doped only with Cr there is one dominating  $\text{Cr}^{3+}$  center, so called center  $\gamma$ . The concentrations of the other centers, encountered in congruent crystals, denoted as centers  $\alpha$  and  $\beta$ , are very low. These centers correspond to Cr ions in  $\text{Li}^+$  sites in  $\text{LiNbO}_3$  host. Another center, denoted as center  $\delta$  becomes dominating in congruent and near-stoichiometric crystals doped additionally with magnesium with appropriate concentration. This center corresponds to  $\text{Cr}^{3+}$  ions in  $\text{Nb}^{3+}$  sites. Much smaller inhomogeneous broadening of R-lines in near-stoichiometric crystals than in congruent ones allow to identify for the R-lines associated with the  $\delta$  center, which became discernible in the luminescence spectra above pressure of 70 kbar. Due to the small inhomogeneous broadening also the position of the  ${}^4\text{T}_2$  level associated with the  $\gamma$  center at ambient pressure can be determined.

At ambient pressure the  $\beta$  and  $\gamma$  centers are the intermediate strength crystal-field centers, although the energy differences between the  ${}^4\text{T}_2$  and  ${}^2\text{E}$  levels are negative for both of them. The Cr ions in the  $\delta$  center experience low strength crystal field at ambient pressure. The R-lines of the  $\beta$  and  $\gamma$  centers exhibit large red shift with pressure of about  $3\text{ cm}^{-1}/\text{kbar}$ . This shift for the  $\delta$  center is equal to about  $1.7\text{ cm}^{-1}/\text{kbar}$ .

Three non-equivalent  $\text{Cr}^{3+}$  centers were found in the LLGG crystal. The  $\text{Cr}^{3+}$  ions experiences in LLGG crystal very low crystal field strength. The energy differences between the  ${}^4\text{T}_2$  and  ${}^2\text{E}$  levels are negative and equal to about  $1400\text{ cm}^{-1}$  for two of those centers and about  $1800\text{ cm}^{-1}$  for the third one.

## Chemical tuning of transition metal upconversion properties

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Upconversion, i. e. short-wavelength emission after photo-excitation at longer wavelengths is a very common and well explored phenomenon among the trivalent lanthanides. More than 30 years of research efforts devoted to this area have ultimately led to application of such materials in laser light sources, imaging materials and IR quantum counters.<sup>1,2</sup>

By contrast, the field of transition metal (TM) upconversion is very young and therefore relatively unexplored. This is mainly due to the fact that emission from multiple excited states, an essential prerequisite for upconversion processes, has so far been observed in only a handful of TM ions. However, an important advantage of such TM upconverters, when compared to the rare earth upconversion ions, is the sensitivity of the spectroscopically active d-orbitals towards their ligand field environments. It allows the experimentalist to tune the photophysical properties of these ions.

By means of chemistry we are capable to control parameters such as the identity of the metastable excited states involved in the upconversion processes, magnetic exchange interactions between TM ions, energy transfer processes between different emitting species, as well as nonradiative multiphonon relaxation rates. The aim of our contribution is to illustrate this versatility of TM upconversion with a few specific example systems, which have recently been explored in our group.

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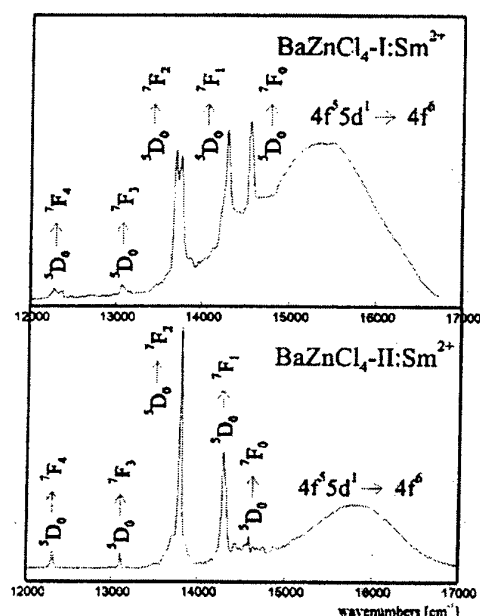
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## Luminescence of $\text{Sm}^{2+}$ in Tetrachlorozincates

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The shape of the emission spectra of  $\text{Sm}^{2+}$ -ions depends very strongly on the host lattice.  $^5\text{D}_J \rightarrow ^5\text{F}_J$  line emission or  $5\text{d}^14\text{f}^5 \rightarrow 4\text{f}^6$  broad band emission or both are observed. While the position of the excited  $^5\text{D}_J$  states are at nearly equal energy the position as well as the metal-ligand-distance of the  $\text{Sm}^{2+}$  doped in different compounds. For the investigation of the shift it is important to investigate nearly equal host lattices where only one crystallographic parameter is changed.



Emissionspectra of  $\text{BaZnCl}_4:\text{Sm}^{2+}$  at 298K

The tetrachlorozincates,  $\text{SrZnCl}_4$  and two modifications of  $\text{BaZnCl}_4$ , are interesting model systems for this problem. The coordination polyhedra of the alkaline earth sites are very comparable, especially  $\text{BaZnCl}_4\text{-I}$  and  $\text{BaZnCl}_4\text{-II}$  show the same coordination number and point symmetry  $\text{C}_2$ . The Ba-Cl-distances differ only approximately 1 pm, causes a shift of the maximum of the  $5\text{d}^14\text{f}^5 \rightarrow 4\text{f}^6$  emission of  $450\text{ cm}^{-1}$ . At lower temperature the shape of the emission spectra changes again: only f  $\rightarrow$  f emission is visible in both spectra. While  $\text{BaZnCl}_4\text{-I}:\text{Sm}^{2+}$  shows  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  emission,  $^5\text{D}_1 \rightarrow ^7\text{F}_J$  emission is observed in the case of  $\text{BaZnCl}_4\text{-II}:\text{Sm}^{2+}$ . This result can be explained by electron transfer processes, which can be investigated with lifetime measurements. The excitation spectra show  $^5\text{F}_0 \rightarrow ^7\text{D}_J$  as well as f  $\rightarrow$  d excitation including a zero-phonon-line, so an exact determination of the energetic position and the change of the metal-

ligand-distance is possible.

In contrast, the larger crystal field of  $\text{SrZnCl}_4$  causes a shift of the lowest  $5\text{d}^14\text{f}^5$  state of  $\text{Sm}^{2+}$  to lower energy, so only  $5\text{d}^14\text{f}^5 \rightarrow 4\text{f}^6$  emission is observed at room temperature while at low temperature line and broad band emission appear.

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## Rare earth-doped $\text{Lu}_2\text{O}_3$ -based X-ray phosphors

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Our interest in  $\text{Lu}_2\text{O}_3$ -based luminophors comes from the fact that it is material of very high absorption coefficient for X-ray radiation. This property makes it possible to use relatively thin layers of lutetia to absorb practically all the incident ionizing radiation [1, 2]. This further gives hope for getting high-quality medical images due to lowering all the negative, light-scattering effects. Even more, since  $\text{Lu}_2\text{O}_3$  is an isotropic compound it can be sintered at temperatures well below its melting point forming bodies of high transparency.

In this communication we will discuss the basic spectroscopic properties of  $\text{Lu}_2\text{O}_3$  doped with Tb or Eu. The materials will be prepared in the form of powders of various mean crystallites sizes as well as in the form of sintered ceramics. Absorption, excitation and emission spectra of the materials will be shown together with the results of emission kinetic measurements.

Emission stimulated with various excitation radiation, among others with X-rays, will be presented and compared. Emission efficiency under X-ray radiation excitation will be compared to that of  $\text{CsI:Tl}$ , the commercial, most efficient scintillator ever found [3, 4]. It will be shown, that only emission from the  $^5\text{D}_0$  level of  $\text{Eu}^{3+}$  and from the  $^5\text{D}_4$  state of  $\text{Tb}^{3+}$  are created, independently on the excitation source. Thus, doping with Eu leads to red emission with the main component at 611 nm ( $^5\text{D}_0$ - $^7\text{F}_2$  hypersensitive transition) and Tb-activation creates green luminescence with two structured bands around 480nm and 545nm.

Emission of Eu-doped samples can be efficiently recorded with CCD cameras, which makes  $\text{Lu}_2\text{O}_3\text{:Eu}$  composition more attractive for digital radiography. Nevertheless, our preliminary experiments seems to indicate that both dopants are able to efficiently compete for the energy deposited in the  $\text{Lu}_2\text{O}_3$  host material by X-ray radiation. While undoped specimens show a defect-related broad-band luminescence it can be totally suppressed by the activators. This also indicates that these activators are very active and efficient in interception of the excitation energy deposited in the material by an incident radiation.

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## Determination of the photodynamic activity of PDT photosensitizers

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In a photodynamic therapy (PDT) process, a reaction takes place when a photosensitizer (PS), light of appropriated wavelength, and oxygen are present at the same time. In general, the PS are porphyrins and related systems [1]. The photodynamic activity (PA) of the PS is related to quantum yields ( $\Phi_{\Delta}$ ) for the singlet oxygen ( $^1O_2$ ) production. Uric acid, a known singlet scavenger, is utilized as a chemical dosimeter in the PDT. When the acid uric (UA) and PS solution is irradiated with laser light the AU band absorbance at 293 nm decreases as a rapid evaluation of relative photodynamic activity of the PS [2].

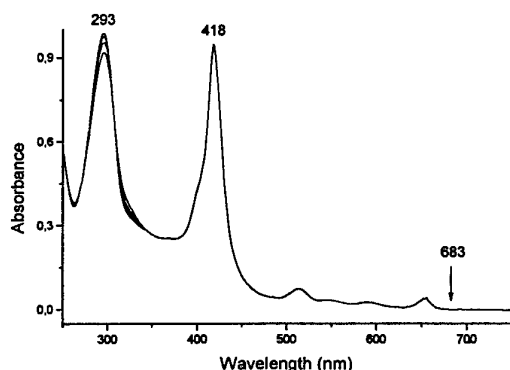
In this work we determined the PA of the Benzoporphyrin (BPH<sub>2</sub>), Protoporphyrin-IX (Proto), Tetrakis(p-hydroxyphenyl)porphyrin (THPPH<sub>2</sub>), Tetrakis(2-hydroxi-5-nitrophenyl)-porphyrin (T2H5NPPH<sub>2</sub>) and Zinc-phthalocyanine (ZnPc), by the method using uric acid (UA) [2, 3]. Irradiations were performed at 683 nm using an MMD-Optics Laser the power of 12,9 W/m<sup>2</sup>. The samples were irradiated, in a quartz cell with solutions containing UA ( $\sim 10^{-3}$  mol.L<sup>-1</sup>) and a PS ( $\sim 10^{-5}$  mol.L<sup>-1</sup>). All measurements were made at 25 °C for 1 hour, in air-saturated solution. The absorbance spectra were registered each 3 minutes in a HP 8543 (diode array) spectrophotometer. The PA values were determinate by the Fischer's expression (1) and are showed in the Table.

$$PA = \Delta A_{UA} \cdot 10^5 / E_0 \cdot t \cdot A_{PS\lambda irr} \quad (1)$$

PA = photodynamic activity;  $\Delta A_{UA}$  = UA absorbance decrease at 293 nm in UA and PS solution after irradiation;  $E_0$  = laser power;  $t$  = irradiation time and  $A_{PS\lambda irr}$  = absorbance of PS in UA and PS solution after irradiation.

**Table.** PA values determinate by the Fischer's expression:

PS	T2H5NPPH <sub>2</sub>	THPPH <sub>2</sub>	Proto	BPH <sub>2</sub>	ZnPc
PA	430	285	230	113	0,58



**Figure:** Absorbance of the UA and T2H5NPPH<sub>2</sub>.

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# POSTERS

## Luminescent features of the sol-gel glasses doped with copper and europium

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A development of new luminescent materials with complex composition is now an actual practical task. It is of interest also for understanding of electronic excitation and relaxation phenomena with participation of two and more active centres. Silica-based optical matrices fabricated by means of the sol-gel technique that provide feasibility to vary optical properties changing concentration and type of dopants in matrix: metal ions, metal clusters and semiconductor nanoparticles.

By this method we have produced the materials in which a number of different mechanisms of relaxation of electronic excitation energy can occur. In the present work, we study luminescent properties of sol-gel silica glasses containing  $\text{Eu}^{3+}$  ions (which are presupposedly in the form of oxide  $\text{Eu}_2\text{O}_3$ ) and (or) copper oxide nanoparticles ( $\text{CuO}$ ) dispersed in the silica matrix. Such materials can be produced both as monolithic glasses of high optical quality and thin films on solid substrates. To fabricate them we introduced  $\text{Eu}^{3+}$  ions into precursor sols within the framework of the modified sol-gel technique based on the catalytic hydrolysis of silicon-organic compounds with subsequent polycondensation of R-Si-O- fragments.  $\text{CuO}$  nanoparticles were prepared from copper salts by their thermal decomposition followed by the  $\text{SiO}_2$ -matrix annealing. The latter process resulted in stabilization of final products and provided a high mechanical strength of materials.

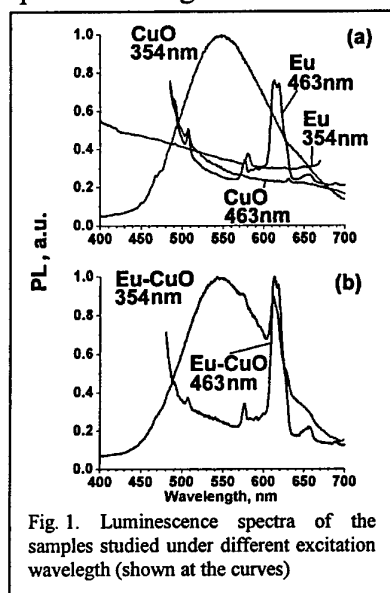


Fig. 1. Luminescence spectra of the samples studied under different excitation wavelength (shown at the curves)

Luminescence spectra ( $T=300\text{ K}$ ) of the sol-gel derived monolithic glasses containing  $\text{CuO}$  nanoparticles with size 50-100 nm and  $\text{Eu}^{3+}$  ions (Fig.1) under excitation at  $\lambda=436\text{ nm}$  reveal the two main emission types: a series of the lines in the range 550-670 nm due to  $\text{Eu}^{3+}$  ions (a series of  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  transitions) and the broad band in the region of 450-650 nm with the maximum at 550 nm. The band at 550 nm presents also in the samples containing *only*  $\text{CuO}$  nanoparticles (Fig.1a). The luminescence spectrum of  $\text{Eu}^{3+}$  slightly changes from the spectrum observed for a samples containing only  $\text{Eu}^{3+}$  ions, the position and the width of the main maximum  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition are preserved, but its splitting disappeared with  $\text{CuO}$ . Meanwhile, under the excitation at 354 nm, at which  $\text{Eu}^{3+}$  ions have no absorption bands, no remarkable luminescence of the  $\text{Eu}^{3+}$  ions observed (Fig.1a). However, in the combined system with  $\text{CuO}$  nanoparticles this signal does appear (Fig.1b).

Thus, excitation of the  $\text{CuO}$  nanoparticle promotes the radiative recombination through participation of  $\text{Eu}^{3+}$  levels with efficiency not less than the proper emission by  $\text{Eu}^{3+}$ . This effect can be of interest for management of luminescent properties of metal ions in silica matrix due to their interaction with absorptive semiconductor nanoparticles.

## Spectroscopic and crystal field studies of $\text{Nd}^{3+}$ in $\text{GdCOB}$ and $\text{YCOB}$ crystals

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In last years a new class of  $\text{Nd}^{3+}$  doped crystals has been developed,  $\text{Nd}^{3+}$ :oxoborates,  $\text{RECa}_4\text{O}(\text{BO}_3)_3$  with  $\text{RE}^{3+}=\text{Y}^{3+}$  or  $\text{Gd}^{3+}$ . Among the advantages of these crystals, besides their good non - linear properties, we mention the congruent melting, large concentrations of the dopant, the possibility to work in various regimes at  $1\mu\text{m}$  or as a self - doubling frequency crystals, e.g. [1, 2].

The purpose of this paper is to analyse the spectral features of  $\text{Nd}^{3+}$  in RECOB crystals. The high purity crystals were grown by Czochralski method in iridium crucible. The low temperature absorption and emission spectra under selective excitation were performed.  $\text{Nd}^{3+}$  ion could replace the  $\text{Gd}^{3+}$  or  $\text{Y}^{3+}$  as well as two  $\text{Ca}^{2+}$  sites in RECOB. The low temperature spectra reveal the presence of a prevailing center, assigned to  $\text{Nd}^{3+}$  in  $\text{RE}^{3+}$  distorted octahedron with  $\text{C}_s$  site symmetry. The absorption and selective emission spectra present also numerous additional lines, connected to other  $\text{Nd}^{3+}$  sites and vibronic sidebands. Vibronic sidebands interfere with main lines in several spectral regions, especially with the following transitions:  $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$ ,  $^2\text{G}_{7/2}$ ;  $^4\text{G}_{7/2}$ ,  $^2\text{K}_{13/2}$ ,  $^4\text{G}_{9/2}$ ;  $^2\text{G}(1)_{9/2}$ ,  $^2\text{D}(1)_{3/2}$ ,  $^4\text{G}_{11/2}$ ,  $^2\text{K}_{15/2}$ . In order to separate zero - phonon lines from vibronics, an analysis of the spectra by using previously reported Raman data [3] was undertaken. The effect of the electron - phonon interaction on the linewidths of zero-phonon lines is discussed.

To elucidate the nature of the satellites accompanying the main  $\text{Nd}^{3+}$  lines, high resolution spectra were recorded on various samples with different dopant concentrations. Different spectral lines were investigated. The site selective excitation in  $^4\text{I}_{9/2}(1) - ^4\text{F}_{5/2}(1)$  line with a Ti: sapphire cw laser pumped by an argon ion laser allows the separation of the emission lines connected to the main  $\text{Nd}^{3+}$  center and to other three perturbed sites in the  $^4\text{F}_{3/2}(1) - ^4\text{I}_J$  transitions. Possible models for additional sites are discussed.

The energy level scheme of experimentally determined Stark levels of the  $\text{Nd}^{3+}$  main site in  $\text{GdCOB}$  are used in a phenomenological crystal field calculation.

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## Crystal field calculations of $\text{Yb}^{3+}$ – doped double borate crystals for laser applications

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Accurate energy level schemes are of crucial importance as far as laser performances of Yb-doped laser materials are concerned. Unfortunately, due to strong vibronic effects and emission / reabsorption processes, it is often very difficult to assign the experimental lines to the electronic levels in Yb-doped laser materials. New Yb-based double borate crystals have been elaborated recently in our laboratory and laser oscillations in these new crystalline hosts have been presented [1]. Nevertheless there is still some uncertainties concerning the positions of the energy levels even if low temperature spectroscopy have been realized.

Two tools are presented as useful facilities in the assignment of the energy levels. First, the so-called "barycenter law" [2] which concerns the position of the barycenter of the  $^2F_{7/2}$  manifold with respect to the position of the  $^2F_{5/2}$  one. Second, calculations are performed using the simple overlap method (SOM) model [3]. Identical values of the adjustable free-ion parameters are chosen for all the double borates. These calculations lead to the determination of the energy level diagram of several Yb doped double borates:  $\text{Sr}_3\text{Y}(\text{BO}_3)_3$  (SrYBO),  $\text{Ba}_3\text{Lu}(\text{BO}_3)_3$  (BLuB),  $\text{Ca}_4\text{GdO}(\text{BO}_3)_3$  (GdCOB) and  $\text{YAl}_3(\text{BO}_3)_4$  (YAB). Some matrices present two local environments for ytterbium cation and a set of crystal field parameters is estimated for each crystallographic site in agreement with the structural data.

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## Crystal field strength in C-type rare earth oxides

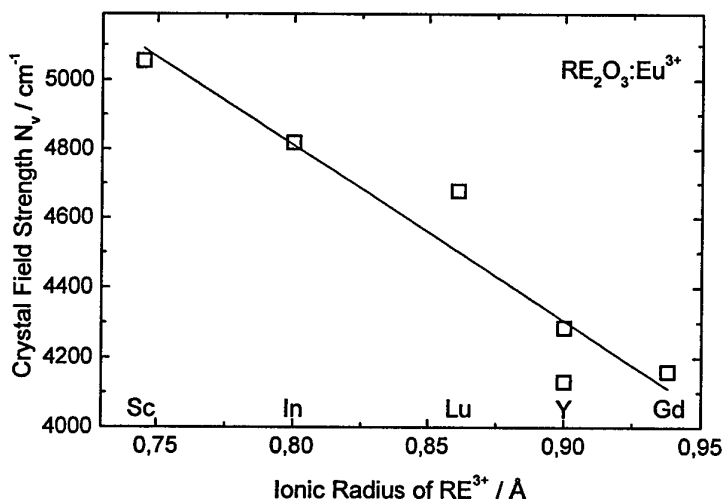
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The rare earth (RE) oxides,  $\text{RE}_2\text{O}_3$ , doped with  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  ions, are important phosphors and precursors for many other, even more widely used luminescent materials. For theoretical studies, the cubic C-type oxides  $\text{C-RE}_2\text{O}_3$  (RE = Eu - Lu, Y, In and Sc) offer a tempting possibility for comparison of luminescence properties because of their extensive structural isomorphism which is rarely encountered even in the RE series [1].

In this work, the luminescence spectra of the  $\text{Eu}^{3+}$  ion in selected C-type rare earth oxides were analysed in detail. The structure-luminescence properties relationships were established by using a phenomenological crystal field (c.f.) simulation of the energy level schemes of the ground  $^7\text{F}_J$  ( $J = 0-4$ ) multiplet. The strength of the c.f. effect – using the parameter  $N_V$  [2] – was related structural stresses due to doping with the  $\text{Eu}^{3+}$  ion. Comparison between the c.f. effect and the external pressure was established.



The c.f. simulations gave satisfactory and consistent results despite the high number of  $B_q^k$  c.f. parameters (15 for the  $C_2$  site symmetry) and low number of levels (18-21). The c.f. strength parameter  $N_V$  decreases with increasing  $\text{RE}^{3+}$  (RE = Gd-Lu, Y, In and Sc) ionic radius although theoretically the c.f. strength should increase in the non-doped  $\text{RE}_2\text{O}_3$  series as shown for the  $\text{REOCl}$  host series [3].

However, when a large

dopant as the  $\text{Eu}^{3+}$  ion is introduced in a smaller host site important dopant-host effect reverses the evolution of the c.f. strength. Other dopant-host effects are presented, as well.

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## Spectroscopy of $\text{Cr}^{3+}$ -doped $(\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2)$ glasses

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$\text{Cr}^{3+}$ -doped glasses in the  $\text{CaO-Ga}_2\text{O}_3\text{-GeO}_2$  family of compositions with high chemical purity and optical quality were obtained through standard high-temperature synthesis methods. The chromium was added to the glass composition in the form of a  $\text{CrCl}_3$  liquid solution at concentrations of 0.01–0.2 wt.%. In this contribution absorption, excitation and high pressure photoluminescence spectra of a glass with the garnet composition  $\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$  are presented. Measurements were performed at pressures up to 150 kbar over the temperature range from 20 K to 293K. Two various centers related to  $\text{Cr}^{3+}$  have been investigated. The first emitting through the broad band with a half width of  $\sim 1700 \text{ cm}^{-1}$  and a peak energy of  $\sim 12700 \text{ cm}^{-1}$  and a sharper band with halfwidth  $\sim 90 \text{ cm}^{-1}$  and a peak energy of  $\sim 14495 \text{ cm}^{-1}$ , and the second that emits mainly by broad band emission peaked at  $10000\text{--}11000 \text{ cm}^{-1}$ . At all- considered temperatures, the sharp emission band exhibited a pressure-induced red shift ( $-1.75 \pm 0.05 \text{ cm}^{-1}/\text{kbar}$ ) that is typical for R-line luminescence in octahedrally coordinated strong field  $\text{Cr}^{3+}$  systems. We accordingly assign the sharp emission band to the R-line ( ${}^2\text{E} \rightarrow {}^4\text{A}_2$ ) transition of  $\text{Cr}^{3+}$  dopands in the glass. Unexpectedly, however, the broad band emission  $12700 \text{ cm}^{-1}$  abbreviates very similar pressure shift as the R line emission. Thus, despite its similarity in appearance to the  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transition of octahedrally coordinated low field  $\text{Cr}^{3+}$ , is not related to this center. We relate them rather to R line phonon sideband that is additionally inhomogeneously broadened by disorder of glass. Since the broad band luminescence at  $10500 \text{ cm}^{-1}$  is pressure independent it is related to strongly distorted  $\text{Cr}^{3+}$  or  $\text{Cr}^{4+}$  sites where the initial compression leads to structural rearrangements of glass network with little or no influence on the local Cr-O bonds lengths.



## Theory and Monte-Carlo simulations of the cooperative concentration quenching kinetics

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Cooperative effects can play an important role in the dynamical processes of optically pumped rare-earth doped materials since they rule excitation quenching processes as well as down-conversion and sensitization energy transfers.

Recently experimental observation of the quadratic concentration quenching rate dependencies and high rate of cooperative energy transfer from Nd, Ho or Tm as a donor ion to the pair of Ce ions as a cooperative acceptor was established [1].

In this paper analytic solution for donor fluorescence decay curve in case of cooperative quenching and averaging over the whole ensemble of statistically distributed ions will firstly presented. The processes under consideration are more complicated, compared with well known process of the energy transfer from donor ion to single-acceptor [2-5], and some assumptions were used here.

Two-acceptor cooperative quenching has also been computer simulated by the Monte-Carlo technique for various ion concentrations. Both the simulated and analytic decay curves plotted in double logarithmic scale of intensity against logarithm of time have at long time a shape similar to nonexponential Forster decay curves for one ion-acceptor quenching. From the slop of the curves, the nonexponential time law was calculated for the various donor-acceptors interaction types [6]. In particular, the nonexponential time low for dipole-dipole interactions of donor with pair acceptors [6] is found to be with power approximately equal 0.4.

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**Anti-Stokes emission in the Nd and Yb doped YAG nanocrystalline ceramics****A. Bednarkiewicz, W. Stręk, D. Hreniak, P.J. Dereń**

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Neodymium and ytterbium doped YAG ceramics were prepared with the concentration ratio of both ions equal to 1/3, 1/5 and 1/10 respectively. Absorption was measured and compared with the absorption of Nd:YAG ceramics. Anti-Stokes and Stokes room and low temperature luminescence spectra were measured under 976 nm and 808 nm excitation. The spectra are characterised with broad lines. Luminescence spectra depended non-linearly on pumping power. Slow rise-time of fluorescence (of an order of seconds) after turning on the excitations source was observed, which slightly depend on concentration ratio and pumping power. The such behaviour are discussed.

### Electrical and optical characterisation of alternate current electroluminescent devices based on ZnS:Cu

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The present study is focused on the electrical and optical properties of ac powder electroluminescent lamps, in which the electroluminescent materials are based on ZnS:Cu, in order to understand the mechanisms of the electroluminescence and improve their performances. To this purpose *ad hoc* sets of devices have been built and their performances have been evaluated by comparing electrical and spectroscopic measurements performed by changing alternatively the applied frequency and the voltage. The emission wavelength of these devices (i.e. the color of the lamps) is found to be strictly related to the applied frequency, while the voltage mainly determines the intensity of the emission. Moreover, a peculiar response of the current-to-tension phase displacement as a function of the frequency has been established. An explanation of these results will be proposed on the basis of changes in the dielectric function of the material due to a polarization effect.

## The spherical micropowders as the precursors for RE<sup>3+</sup>-doped silica gel-glass preparation

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The synthesis of spherical micropowders doped with rare-earth elements (RE) ions promising for industrial preparation of optical silica glasses.

The process of doped silica powders preparation incorporates the hydrolysis of tetraethylorthosilicate in the system  $\text{Si}(\text{C}_2\text{H}_5\text{O})_4\text{-H}_2\text{O-NH}_4\text{F-(CH}_2)_6\text{N}_4$ , introduction the sel of RE<sup>3+</sup> ( $\text{MCl}_3\cdot 6\text{H}_2\text{O}$ ) into the sol, gelation in the period of 30 min, drying and presintering at 600°C in 8 hours. The incorporation of fluorine into the reaction mixture catalyses the hydrolysis process and reduces bubble formation up on consolidation at high temperature.

The using of hexamethylenetetramine in the process of silica spheres preparation results in the formation of supramolecular complex  $\text{LnCl}_3\cdot[(\text{CH}_2)_6\text{N}_4]\cdot 12\text{H}_2\text{O}$  in the intermicelleous space under thermo-treatment.

For preparation of porous green bodies the method of cold pressing and slurry molding were utilized. The diameter of spherical particuls was 0,5–1,5 μ with narrow size distribution. The following thermo-treatment of RE<sup>3+</sup>-containing porous materials at the temperature 1200–1350°C on air lead to formation of porous silica glass. The using of hydrogen-oxygen flame is required for consolidation the green bodies into clear doped gel-glass.

The mechanism of doping via process of complex formation is considered as well as the models of RE<sup>3+</sup>-ions behavior in silica network.

The optical and luminescent properties of gel-glasses doped with Er<sup>3+</sup> ions as well as REM investigations is considered in the paper.

## Magnetic properties in the heteronuclear $\text{CuNd}_2$ and $\text{CuSm}_2$ systems and their simple Nd and Sm analogues

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The mechanism of magnetic interaction in heteronuclear (f- and d- electron) systems has been not satisfactorily explained yet. The results presented in this paper can add to the data from this field and may throw light on some aspects of this important problem.

The series of the heteronuclear compounds  $\text{CuLn}_2(\text{CCl}_3\text{COO})_8 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Nd}$  and  $\text{Sm}$ ) and their simple analogues ( $\text{Nd}$ ,  $\text{Sm}$ ) were obtained. Molecular structures were determined by X-ray diffraction [1,2]. Magnetic susceptibilities were measured in the range 300-1.7 K [3] and in the function of magnetic field.

Untypical hysteresis was found (two loops) in samarium trichloroacetate. This phenomenon is most probably the effect of moving spins in magnetic fields of 30000 Oe. A similar magnetic behaviour was observed in neodymium carboxylate where at low temperature (1.6 K) the magnetic ordering was observed as a result of Nd-Nd interaction. For that system, at low temperatures, the magnetic moment depends on the magnitude of the magnetic field and ferromagnetic ordering appears. The strongest interactions of coupled ions and antiferromagnetic ordering with  $T_N = 6.5$  K were found in the  $\text{CuSm}_2(\text{CCl}_3\text{COO})_8 \cdot 6\text{H}_2\text{O}$  single crystals.

The calculations of the magnetic susceptibilities for the series of title systems were made depending on the temperature in the 1-10 K range. The Heisenberg model was applied in the calculations for three interacting ions located linearly. The following relation was derived:

$$\chi_M = N \frac{g^2 \mu_B^2}{kT} \cdot \frac{\left(\frac{1}{2}\right) + \left(\frac{1}{2}\right) \exp(J_2/kT) + 5 \exp(J_2/kT) - \exp(1,5J_1/kT)}{2 + 2 \exp(J_2/kT) + 4 \exp(J_2/kT) - \exp(1,5J_1/kT)}$$

and applied in calculations of the exchange integrals. On the basis of the obtained results the mechanism of the exchange interaction was discussed.

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## Spectroscopic and magnetic studies of mixed lanthanide complexes: $\text{LnL}_3\alpha,\alpha\text{Dipy}$ in solution, solid and gel

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The investigation of lanthanide chelates with  $\beta$ -diketonates and their derivatives is being actively pursued because of possibilities of their applications. They are applied in anticancer treatments, NMR shift reagents and luminescence labels in fluorimetric analysis. The most interesting are mixed lanthanide complexes with general formulae  $\text{LnL}_3\text{Y}$  with two types of ligands, where L-is a  $\beta$ -diketonate, Y- is Lewis base such as dipyridyl or 1,10-phenanthroline for which efficiency of energy transfer could be expected.

The monomeric complexes  $\text{LnL}_3\alpha,\alpha\text{Dipy}$  were synthesized ( $\text{Ln} = \text{Eu}^{3+}, \text{Tb}^{3+}, \text{Yb}^{3+}$ ); L – phosphoro-azo derivative of  $\beta$ -diketonate:  $\text{CCl}_3\text{C}(\text{O})\text{NP}(\text{O})(\text{OCH}_3)_2$  and  $\alpha,\alpha\text{Dipy}$  –  $\alpha,\alpha$ dipyridyl and their single crystals were grown up. X-ray diffraction studies were done. The complexes crystallizes in the monoclinic system, space group C2/c for Er(III) and triclinic, P1 for Eu(III) and Tb(III). The compounds were incorporated into silica gels to increase their efficiency of interion emission. The magnetic susceptibility and magnetization of crystals were investigated. High resolution absorption, luminescence and excitation of luminescence spectra were measured for crystals and gels at 293, 77 and 4 K in order to characterize their physical properties. Radiative and nonradiative processes will be analyzed. The role of ligand singlet and triplet states in energy-transfer as well as charge-transfer states in emission quenching were studied.

## C-F calculation, optical and magnetic characteristics of lanthanide chelate dimer systems

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The lanthanide chelates with two types of ligands are the subject of wide research because of their relevance in solid-state technology. They can be applied in synthesis of nanosize systems and can be used in technology of electroluminescence diodes. A number of important characteristic of these materials can be correlated with the donor-acceptor properties of the substituents of ligands. Furthermore they affect the electron-phonon coupling, energy transfer and quantum yields of the luminescence. On the other hand the dimer systems are the model to study of M-M interaction and its effect in spectral and magnetic properties.

The single crystals of dimeric compounds:  $\text{Ln}(\text{C}_5\text{H}_{11}\text{COO})_3\text{Phen}$ , where  $\text{Ln}=\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Phen}=1,10$  phenanthroline, were synthesized. The neodymium complex crystallizes in monoclinic system, space group  $\text{P2}_1/\text{n}$  with lattice parameters:  $a=15.975(2)$  Å,  $b=12.714(2)$  Å,  $c=16.539(2)$  Å,  $\beta=110.76^\circ$  and  $Z=4$  [1]. The  $\text{Eu}(\text{C}_5\text{H}_{11}\text{COO})_3\text{Phen}$  is isomorphous with neodymium one. The lanthanide ion occupy one symmetry site in centrosymmetric dimeric unit. The distorted monocapped square antiprism are formed, where the metal ion is coordinated with seven oxygen atoms of carboxyl groups and two nitrogen atoms of phenanthroline.

High resolution absorption and luminescence spectra were measured at 298, 77 and 4 K to characterize their optical properties. Excited states dynamic was studied and the role of ligand singlet and triplet states and C-T states on efficiency of lanthanide emission have been analyzed. The set of the CF Stark components were used in the CF calculations. The energy levels diagram was determined and satisfactory correlation between experimental and calculated levels were found. On the basis of obtained results the magnetic susceptibility were calculated for europium(III) and neodymium(III) systems. The calculated results quite good reproduce observed experimental values. The changes of magnetic susceptibility and magnetic moment with temperature are analyzed in the frame of weak M-M interaction scheme.

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## Optical spectra of yttrium phosphate and vanadate single crystals activated with Dy<sup>3+</sup>

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Up to a recent past, Dy<sup>3+</sup> has not been considered among the most important laser ions, such as Nd<sup>3+</sup>, Er<sup>3+</sup>, Ho<sup>3+</sup>, etc. Studies on the optical properties of some oxide crystals doped with Dy<sup>3+</sup> ions were carried out in order to develop solid state lasers in the 3  $\mu$ m region using the <sup>6</sup>H<sub>13/2</sub> → <sup>6</sup>H<sub>15/2</sub> channel [1, 2]. However, it is evident that in most of these materials this laser transition would be strongly affected by multi-phonon relaxation processes related to high energy (800-900 cm<sup>-1</sup>) vibrational modes. For this reason, they were not considered to be very interesting for the solid state laser technology. In 2000 Kaminskii et al. have [3] reported laser action of Dy<sup>3+</sup>-doped tungstates in two novel laser channels, <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> (yellow) and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>11/2</sub> (red), at liquid nitrogen temperature under Xe-flashlamp. This opens new perspectives for the technological application of these materials, so we have decided to undertake a systematic study on the optical properties of oxide crystals activated with Dy<sup>3+</sup> in order to evaluate their potentialities as visible lasers. Here we present the results of our investigations on YPO<sub>4</sub>:Dy and YVO<sub>4</sub>:Dy. The absorption spectra have been measured at 10 and 298 K using polarized light. The luminescence spectra have been measured at 10 and 298 K: they are dominated by a strong emission in the 575 nm region. Other bands have been observed in the 480, 665, 750 and 840 nm regions. They have been assigned to transitions from the <sup>4</sup>F<sub>9/2</sub> to lower states on the basis of the energy levels scheme deduced from the 10 K absorption spectra. The intensities of the bands in the room temperature spectra have been analysed using the Judd-Ofelt parametrization scheme, and the  $\Omega_{2,4,6}$  intensity parameters have been determined. Using these data we have then calculated the radiative lifetime and the branching ratios for the emission from the <sup>4</sup>F<sub>9/2</sub> level. The lifetime of the emitting level has been deduced from pulsed light measurements carried out at different temperatures, and the efficiency of the non radiative processes is evaluated and discussed.

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## Spectroscopic and magnetic studies of the ternary praseodymium chloride $\text{K}_2\text{PrCl}_5$

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$\text{K}_2\text{PrCl}_5$  crystallizes with the centrosymmetric space group  $\text{Pnma}$  with the lattice constants  $a = 1263.1(8)$ ,  $b = 875.6(3)$ ,  $c = 797.3(4)$  pm [1]. The structure consists of monocapped trigonal prisms  $[\text{PrCl}_7]$  which are connected via two common edges to form infinite chains running along the crystallographic  $b$  axis. The chains are arranged like a hexagonal packing of rods and are held together by  $\text{K}^+$  ions. The coordination numbers for the metal ions are 7 ( $\text{Pr}^{3+}$ ) and 8+1 ( $\text{K}^+$ ). The intrachain  $\text{Pr}^{3+}$ - $\text{Pr}^{3+}$  distances are all equal at 455.0(2) pm.

The optical and magnetic properties of  $\text{K}_2\text{PrCl}_5$  were investigated in the 1.7 to 293 K temperature range and are discussed on the basis of the X-ray structure data. High-resolution absorption, emission, and excitation spectra as well as decay time measurements at 293, 77, and 4 K are presented and used to characterize the excited state photophysics of  $\text{K}_2\text{PrCl}_5$ . Magnetic susceptibility measurements were carried out down to 1.7 K in both the low and high field regime. Changes of the magnetic moment with temperature are discussed on the basis of the structural data. Spectroscopy and magnetism of  $\text{K}_2\text{PrCl}_5$  are related to respective results of other polymeric systems and are correlated with EPR data.

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**Structure, photophysics and magnetism of europium mixed complex;  
Eu(HFAA)<sub>3</sub>bipy·H<sub>2</sub>O, in solid state, solution and gel**

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Lanthanide  $\beta$ -diketones were used recently in organic-layered electroluminescence diodes (OLEDs) and other applications.

An important characteristics of these materials can be correlated with donor-acceptor properties of the substituents in ligands. Besides, donor-acceptor properties influence the location of ligand singlet and triplet states, as well as the CT state, controlling the energy transfer and efficiency of lanthanide emission.

X-ray data of title compound show that the compound forms triclinic crystals with  $\overline{P}_1$  space group and following unit-cell constants;  $a=11.841$ ,  $b=12.010$ ,  $c=15.054$  and  $\alpha=82.60$ ,  $\beta=88.507$ ,  $\gamma=79.207$ .

Europium ion is coordinated by six oxygen atoms of hexafluoroacetone, two nitrogen of dipyriddy and one water molecule. Besides, one non-coordinated dipyriddy is located in crystal lattice which is disordered over two positions.

Absorption, emission and emission excitation spectra at 293, 77 and 4K, as well as luminescence decay time measurements are used to characterize the title compound in the solid state, solution and gel. The emission properties were strongly dependent on energy of excitation beam and temperature. Magnetic susceptibility measurements were carried out down to 1.7 K. Correlation of the spectra and magnetic properties with details of the structure of the title compound was studied. Careful analysis of spectroscopic characteristics of the title compound permits determination of the applicability of this type of Eu(HFAA)<sub>3</sub>bipy·H<sub>2</sub>O–diketone and makes possible understanding of the mechanism of energy transfer processes. These results are compared with previously reported data of related systems.

## **Spectroscopy of glasses doped with $\text{Sm}^{+3}$ ions**

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Spectroscopic properties and up-conversion in  $\text{KYb}(\text{WO}_4)_2:\text{Ho}^{3+}$ P.J. Dereń<sup>a</sup>, A.A. Demidovich<sup>b</sup>, J-C. Krupa<sup>c</sup>, W. Stręk<sup>a</sup><sup>a</sup>*Instytut Niskich Temperatur i Badań Strukturalnych PAN, ul. Okólna 2, Skr. Pocz. 1410, 50-950 Wrocław 2, Poland, E-mail: deren@int.pan.wroc.pl*<sup>b</sup>*Laser Spectroscopy Laboratory, Institute of Molecular and Atomic Physics, F. Skaryna ave. 70, Minsk, 220072, Belarus*<sup>c</sup>*Institut de Physique Nucleaire, CNRS, IN2P3, 91406 Orsay Cedex, France*

Double tungstate crystal is a very interesting host for Rare Earth ions. Firstly Rare Earth ions' absorption bands are broader than in YAG for example. This is very beneficial when a laser crystal is excited by a laser diode, which emission wavelength changes with temperature. Secondly the double tungstates being monoclinic offers another advantageous feature – they are non-linear. These properties allowed obtaining in the double tungstates doped with  $\text{Nd}^{3+}$  self-stimulated Raman scattering [1].

Holmium is also widely investigated nowadays; it is an interesting ion for anti-Stokes emission including photon avalanche upconversion [2].  $\text{KGd}(\text{WO}_4)_2:\text{Ho}^{3+}$  double tungstate was successfully used to obtain stimulated emission in the IR [3]. The reader will find a preliminary report on  $\text{KYb}(\text{WO}_4)_2:\text{Ho}^{3+}$  in [4].

To enhance emission's quantum efficiency Yb is added into crystals as a sensitizer, the strong  $\text{Yb}^{3+}$  absorption band match very well the emission of IR laser diodes.

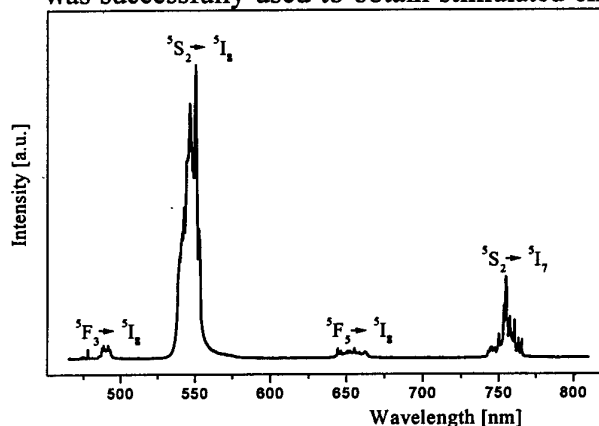
In this work we present the results of investigations of  $\text{KYb}(\text{WO}_4)_2:\text{Ho}^{3+}$  (0,6 %). The single crystal was excited either by pulse IR excitation at 1064 nm and cw excitation at 989 nm. Both excitations produces strong up-conversion emission of  $\text{Ho}^{3+}$  ions in the red and green region, a strong IR emission was observed as well. The peaks are observed at 476.8 nm, 545.6 nm, 658 nm and at 754 nm (the  $^5\text{F}_3 \rightarrow ^5\text{I}_8$ ,  $^5\text{S}_2 \rightarrow ^5\text{I}_8$ ,  $^5\text{F}_5 \rightarrow ^5\text{I}_8$  and the

$^5\text{S}_2 \rightarrow ^5\text{I}_7$  transition respectively). At 2058 nm the  $^5\text{I}_7 \rightarrow ^5\text{I}_8$  transition is observed. Decay time of the green anti-Stokes emission is multi exponential; three components were found 154  $\mu\text{s}$ , 320  $\mu\text{s}$  and 6.4 ms. A characteristic for energy transfer up-conversion rise time of 70  $\mu\text{s}$  was observed as well.

The possible mechanisms of observed anti-Stokes emission are discussed.

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Up conversion emission spectrum of  $\text{KYb}(\text{WO}_4)_2:\text{Ho}^{3+}$ ,  $\lambda_{\text{exc}} = 1064 \text{ nm}$ ,  $T = 300 \text{ K}$ .

## New paths of excitation of up-conversion emission in $\text{LaCl}_3: \text{U}^{3+}$

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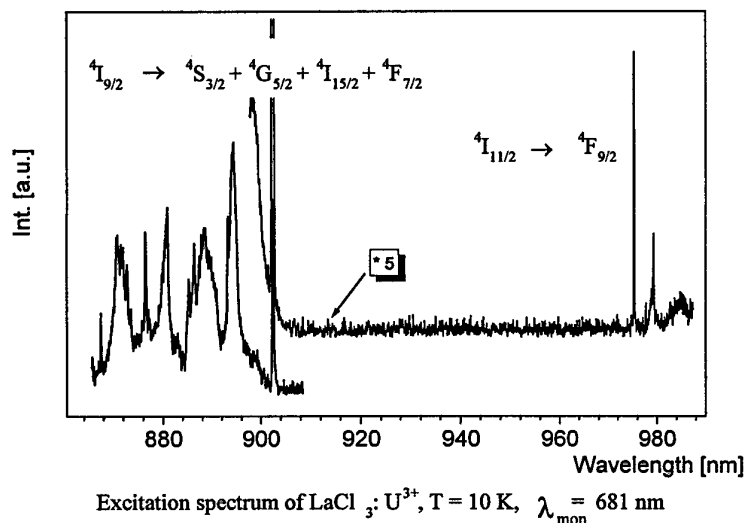
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Actinides, for their unique spectroscopic properties, are very interesting ions for investigations. The 5 f electrons are not so well shield by outer orbitals like in the case of Rare Earth ions. As a result the absorption and emission lines are broadened due to stronger coupling to the crystal lattice, their oscillator strengths are bigger than of Rare Earth ions [1]

Anti-Stokes emission could be obtained in different mechanisms i.e. Two Photon Absorption (with and without an intermediate level), Energy Transfer Up-conversion and Photon Avalanche Up-conversion. Being very useful when converting lower excitation photons into higher energetic ones brings also information about the levels not accessible in one photon absorption spectroscopy. However, there are only few reports on anti-Stokes emission in the actinides [2].



In this paper we report on anti-Stokes emission obtained in  $\text{LaCl}_3$  doped with  $\text{U}^{3+}$  ions. The single crystal was excited in the IR by wavelengths resonant with transitions between excited levels. Such an excitation was chosen because we were looking for a photon avalanche up-conversion not reported yet for the actinides. After cw excitation at 975.3 nm, 977.7 nm and 979.4 nm a strong green and red emission was observed at 10 K. The absorption and emission spectra at low temperatures are reported. An exact examination of the excitation spectra shows however their dependence on monitored emission. Some lines disappeared when monitored monochromator was tuned from the red to the green emission of  $\text{LaCl}_3: \text{U}^{3+}$ . Possible mechanisms of the up-conversion observed as well as a possibility of the photon avalanche up-conversion are discussed.

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## Spectroscopic investigation of the $\text{Ca}_4\text{GdO}(\text{BO}_3)_3$ (GdCOB) crystal singly doped with $\text{Eu}^{3+}$ and $\text{Tb}^{3+}$ ions

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A detailed study of optical properties of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  single doped the  $\text{Ca}_4\text{GdO}(\text{BO}_3)_3$  crystal is presented. Based on low temperature absorption, excitation and emission spectra crystal field levels of active ions have been located. The  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition was used to test the number of non-equivalent sites of  $\text{Eu}^{3+}$  in the  $\text{Ca}_4\text{GdO}(\text{BO}_3)_3$  crystal. Site-selective excitation into the  $^5\text{D}_2$  region has shown the existence of three  $\text{Eu}^{3+}$  crystal-field sites. For the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  emission three lines, observed at 17289, 17308 and 17330  $\text{cm}^{-1}$ , are presented in Fig. 1. The decay times of the observed lines have been measured at 5 K.

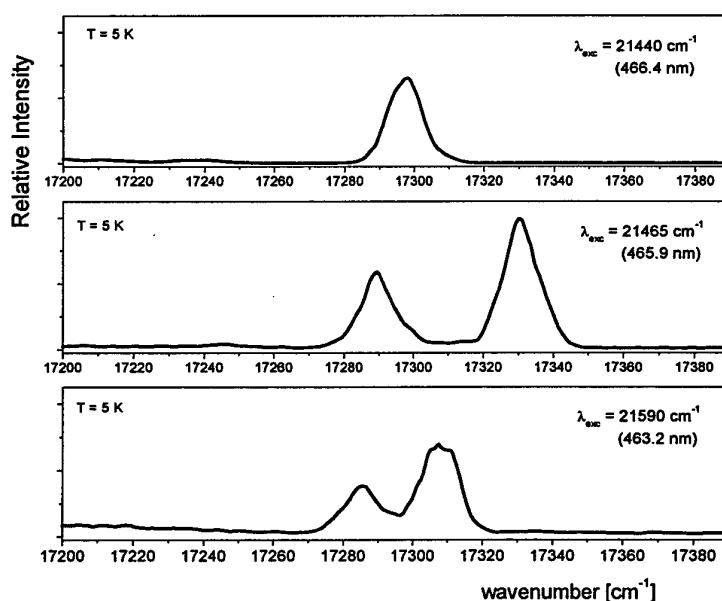


Fig.1. The  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  emission of  $\text{Eu}^{3+}$  in the GdCOB crystal taken at 5 K for different excitation wavelengths: 466.4, 465.9 and 463.2 nm.

According to crystal structure of GdCOB there are three cationic sites:  $\text{Gd}^{3+}$ ,  $\text{Ca}^{2+}$  (Ca1) and  $\text{Ca}^{2+}$  (Ca2). The  $\text{Gd}^{3+}$  and Ca1 occupy six-coordinated sites with  $\text{C}_s$  symmetry whereas, the Ca2 ions occupy eight-coordinated sites with  $\text{C}_3$  symmetry. The existence of three  $\text{Eu}^{3+}$  sites indicates that although  $\text{Eu}^{3+}$  ions are first expected to replace  $\text{Gd}^{3+}$ , a substitution of other cationic sites is possible.

## Crystal-field analysis of $U^{3+}$ ions in $LaCl_3$ , $UCl_3$ and $UF_3$

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High resolution polarised absorption spectra of  $LaCl_3:U^{3+}$  single crystals as well as unpolarised spectra of thin films of  $UCl_3$  and  $UF_3$  have been recorded at 4.2 K. The energy level structure of  $U^{3+}$  in  $LaCl_3$  have been analysed, revised and utilised for assignment of transitions observed in the spectra of  $UCl_3$ . The energy levels of the  $U^{3+}$  ion in the compounds were fitted to semiempirical Hamiltonian employing free-ion operators, one-electron crystal-field operators as well as two-particle correlation crystal-field (CCF) operators. The effects of selected CCF operators on the splitting of some specific  $U^3$  multiplets have been investigated.

On the basis of the obtained electronic wave functions the electric-dipole intensity parameters of the total transition dipole strength were determined by fitting the calculated and experimental transition intensities.

## Thermoluminescence studies of $\text{LaGaO}_3$ crystals

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Lanthanum orthogalate crystals ( $\text{LaGaO}_3$ ) are used as material for epitaxy of high temperature superconductor. Recently this material is investigated as materials for optoelectronics devices. Moreover it was found to be a good material for electrolyte in solid oxide fuel cells.

We have performed investigation of undoped bulk  $\text{LaGaO}_3$  crystals grown by Czochralski method using thermoluminescence technique in 10–400 K temperature range. Several thermoluminescence peaks with activation energies from 0.1 to 1.4 eV were observed.

It was shown that optical spectrum of thermoluminescence in whole investigated temperature range correspond to unknown defect which emits in 690-720 nm spectral range, with maximum near to 712 nm. This emitting center most probably related to unintentional Cr doping, that is present in investigated samples.

We propose a model of energy transfer between the traps and emitting defect in these crystals.



## Spectroscopic study of azide complex of europium in water solution

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Taking into regard the earlier established long-lived chemiluminescence of  $\text{Eu}^{3+}$  in the system  $\text{Eu}^{3+}/\text{N}_3^-/\text{H}_2\text{O}_2$ , spectrophotometric and spectrofluorimetric studies of  $(\text{EuN}_3)^{2+}$  complex formed in the system  $\text{Eu}^{3+}/\text{N}_3^-$  in water solution were undertaken. The absorption spectrum of the solution obtained as a result of the reaction between the solutions of  $\text{EuCl}_3$  and  $\text{NaN}_3$ , revealed two bands. The first one in the short-wavelength range of the spectrum ( $\lambda \sim 200 - 270$  nm) was assigned to ions, whereas the other, with a maximum at  $\lambda \sim 320$  nm was assigned to  $\text{Eu}^{2+}$  ions appearing as a result of  $\text{Eu}^{3+}$  ions reduction by azide ions.

The use of the competitive ligands, i.e. aminopolycarboxylic acids (APA) driving out  $\text{N}_3^-$  ions from the coordination sphere of the europium ions, and the known value of the stability constant of the azide complex of europium, it has been shown that the process of reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ions occurs mainly in the molecule of  $(\text{EuN}_3)^{2+}$ .

The results of the spectrofluorimetric study of  $(\text{EuN}_3)^{2+}$  solutions at  $\lambda_{\text{exc}} = 395$  nm,  $\lambda_{\text{em}} = 595$  and 620 nm, have proved the quenching of  $\text{Eu}^{3+}$  ions emission by  $\text{N}_3^-$  ions and allowed a determination of the Stern-Volmer quenching constant.

## Spherical unhydrous silica particles doped with $RE^{3+}$ -ions as the precursors for silica gel-glass preparation

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Silica spherical particles, doped  $RE^{3+}$ -ions, gained an increasing attention in the recent years, because they offer the possibility of producing a wide variety of unusual materials with interesting properties for applications in heterogeneous catalysis, ceramic glasses, a paint reflection film and a glass precursor [1, 2].

Sol-gel processes were widely applied for their preparation and much attention was paid to optimize preparation conditions and compare methods [3,4]. The silica source may be either a siliciumalkoxide (TEOS) or a concentrated sodium silicate solution (water-glass). The aim of the present work is to obtain a oxide powder material, implies the achievement of spherical shape and a sharp particle size distribution, preferably centered in the mm ranges.

Silica spheres can be prepared by a sol-gel process by hydrolysis and polycondensation of tetraethylorthosilicate in the system:  $Si(C_2H_5O)_4-H_2O-HCl-NH_4F$  at constant mixing. Drying the silica spheres at temperatures  $\sim 100^\circ C$  leads to a lower shrinkage, and consequently to a higher pore volume of the dried spheres. The most essential limitation of the sol-gel silica spheres is a high concentration of OH-groups which are principal technological factor decreasing the luminescence quantum yield of  $RE^{3+}$ -doped silica structures and at application as glass precursor. A significant decrease in the hydroxyl ions concentration was realised thermal treatment of silica spherical particles in fluor/oxygen atmosphere at  $1000^\circ C$ . The content of OH-ions in silica spheres, doped rare-earth ions was  $\sim 50$  ppm. The silica spheres were consolidated into monolithic spherical bodies in air atmosphere at  $1350^\circ C$ . Such of spherical powders can be applied as precursor for preparation doped silica gel-glasses.

Samples were examined by scanning electron microscopy in order to observe the shape and morphology of the particles. The effect of the drying temperature on the pore structure of spherical silica was investigated.

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## Comparison of terbium photoluminescence from ion implanted and sol-gel derived films

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Doping with terbium is widely used for fabrication of green light-emitting phosphors. In this work, we investigate the photoluminescence (PL) of terbium-doped films fabricated by ion implantation and sol-gel synthesis. Terbium implantation was performed into SiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> thin film fabricated by dry processes onto silicon or sapphire substrates followed by heat treatment in vacuum at a temperature ranging from 473 to 873 K during 30 min. Sol-gel-derived films were fabricated onto porous anodic alumina and monocrystalline silicon substrates by spin-on deposition of titania or alumina-based sol containing aqueous-alcohol solution of terbium nitrate. Photoluminescence measurements were carried out at a temperature from 10 to 300 K. Comparison of PL data obtained from Tb-implanted SiO<sub>2</sub>, ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films allows conclusion that ZrO<sub>2</sub> is the best host material for Tb<sup>3+</sup> ions, revealing a set of sharp well resolved bands corresponding to <sup>5</sup>D<sub>4</sub>-<sup>7</sup>F<sub>j</sub> electron transitions of Tb<sup>3+</sup> ions with the maximum at 545 nm. It was found that temperature dependence of Tb-related PL depends on the type of Tb host matrix. Moreover, Tb-doped alumina and titania xerogels fabricated on monocrystalline silicon and porous anodic alumina revealed that exploiting of porous anodic alumina gives a much lower temperature quenching of Tb PL. For any registration temperature, Tb PL was found to be 15-20 times stronger for xerogels fabricated onto porous anodic alumina of 30 micron thick in comparison with ion implanted thin films. Evaluation of mechanism of PL enhancement by porous media is in progress.

## Spectroscopic studies of lanthanide (Ce, Eu) chlorides in ethane-1,2-diol

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Recently we reported attempts to application of spectroscopy in studies of the structure of solutions of cerium and praseodymium chlorides in alcohol solutions [1, 2]. The present investigations are a consequence of them, especially in the aspect of gel and glass formation using hydrolysis of TEOS in nonaqueous media.

The aim of this study is focusing on the spectroscopy of Ce and Eu chlorides in ethylene glycol solutions at 293 and 77 K.

Structure of liquid glycol is supposed to be basically similar to that of water because of formation of relatively strong hydrogen bonds and creation of locally ordered structures. The effect of lanthanide ions on this structure and solvation of them by glycol molecules were investigated using ultrasonic methods, but the results were different than those obtained recently for Ce(III) and Pr(III) chlorides in n-propanol [3].

Eu(III) can be applied as a spectroscopic probe of solution structure. The f-d transitions of Ce(III) in absorption spectra and their correlation with the excitation and emission ones can characterize the spectroscopy of glycol systems containing both anhydrous and hydrated salts.

Thus, we will describe the best spectroscopic conditions of formation of glass codoped by active lanthanide ions. The role of strength of M-solvent interactions on the splitting and energy of f-d transitions will be discussed and related to the earlier reported data. The non-radiative processes in the systems under investigation will also be considered.

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## Optical properties of $\text{YVO}_4$ single crystals doped with $\text{Er}^{3+}$ , $\text{Ho}^{3+}$ , $\text{Tm}^{3+}$

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Single crystals of yttrium orthovanadate have been obtained for the first time thirty years ago. It has been then demonstrated that neodymium doped  $\text{YVO}_4$  displays excellent spectral and laser properties, among others unusually the high stimulated emission cross section and strongly polarised emission. However, application of rare earth doped  $\text{YVO}_4$  has been hampered by poor optical quality of crystals due to defect of valency state of vanadium. It has been even concluded that the Czochralski growth method can not produce laser quality crystals.

Recently, the crystal growth technique has been considerably improved, and the crystals obtained became sufficiently good to achieve laser oscillation in  $\text{YVO}_4$ : Er at room temperature.

In this work the spectroscopic properties of  $\text{YVO}_4$  singly doped with erbium, holmium and thulium are considered. Energies of crystal field levels have been determined based on low temperature absorption and emission spectra. Contribution of radiative transitions, multiphonon relaxation and activator-activator interaction to the decay of excited states has been estimated. Stimulated emission cross sections for laser transitions in near IR region have been assessed.

## Jahn-Teller effect in Co doped SrLaGaO<sub>7</sub>

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We have presented spectroscopic investigations of the Co<sup>2+</sup> in SrLaGa<sub>3</sub>O<sub>7</sub>. Single crystals of SrLaGa<sub>3</sub>O<sub>7</sub> have been grown by Czochralski method in a nitrogen atmosphere. The absorption spectra were taken at various temperature from 2K to 300K in the spectral range 190-2500 nm. It has been found that the Co<sup>2+</sup> ions substitute octahedrally coordinated Sr<sup>2+</sup> in the material. The crystal field splits the sevenfold degenerate <sup>4</sup>F state into an orbital triplet <sup>4</sup>T<sub>1</sub>, followed by another orbital triplet <sup>4</sup>T<sub>2</sub> and an orbital singlet <sup>4</sup>A<sub>2</sub>. The next higher state of the free Co<sup>2+</sup> ion yields in crystal field the <sup>4</sup>T<sub>1</sub>(<sup>4</sup>P) configuration. We have estimated the quantities of the crystal field parameter 10Dq, Racach parameters B and C and spin-orbit coupling. For consideration of the absorption lineshape we have taken into account the coupling of localised electrons to the symmetrical a<sub>1</sub> mode and Jahn-Teller coupling of the  $T \otimes \varepsilon$  and  $T \otimes \tau$  types. Absorption line shapes has been reproduced considering one, two and three dimensional vibronic overlap integrals. We have take into account the non-linear electron-lattice coupling resulting from the spin-orbit interaction. The analysis of the line shape of the <sup>4</sup>T<sub>1</sub>→<sup>4</sup>T<sub>2</sub> and <sup>4</sup>T<sub>1</sub>→<sup>4</sup>T<sub>1</sub> transitions showed that the dominant is effect is the Jahn-Teller  $T \otimes \tau$  coupling in the ground <sup>4</sup>T<sub>1</sub> state of the system. We have estimated the Jahn-Teller stabilisation energies in all considered states. The procedure of estimation of the crystal field strength parameter 10Dq for the system that is affected by strong Jahn-Teller coupling has been discussed.

## Chemical and magnetic properties of the new copper(II) complexes with alkylaminoacetylureas

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New copper(II) complexes with alkylaminoacetylurea ligands have been synthesized. Their chemical compositions have been established. The oxidation state of the complexing copper ion has been analyzed by means of magnetic and ESR studies, performed in a large temperature range. The influence of the ligand dimension on the magnetic properties is discussed. The structure of the complexes studied has been proposed.

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**Temperature dependent ESR studies on the  $\text{Cr}^{3+}$  ion doped  
 $\text{KAl}(\text{MoO}_4)_2$  crystal**

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Temperature-dependent ESR study of  $\text{Cr}^{3+}$  ion in potassium aluminium double molybdate ( $\text{KAl}(\text{MoO}_4)_2$  crystal) are reported. The trigonal chromium complex possess spin Hamiltonian parameters:  $g_{\parallel} = 1.9781$ ,  $g_{\perp} = 1.9727$  and  $|D| = 0.4798 \text{ cm}^{-1}$ . The temperature behaviour of the resonant lines indicates possibility of two phase transitions which take place below 80 and 50K.



## Optical properties of $\text{Nd}^{3+}$ doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ nanoceramics

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The neodymium-doped yttrium aluminum garnet (Nd:YAG) nanocrystalline powders were prepared by sol-gel method. The synthesis of semi-transparent ceramics is described. Their structure and morphology were studied by means of XRD and TEM methods. It was found that with increasing thermal heating the size of Nd:YAG grains increase. The optical properties of  $\text{Nd}^{3+}$ :YAG nanocrystalline powders and ceramics are reported. The effect of grain size on luminescence properties was observed.

## Preparation and Optical Properties of Nanostructured Europium Doped $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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Europium-doped nanostructured monolithic alumina matrix was prepared by the alkoxide sol-gel method. The Eu<sup>+3</sup> ions were introduced by impregnation method and the resulting  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:Eu<sup>+3</sup> samples were heat-treated under the presence of gaseous components from oxidative pyrolysis of polytetrafluoroethylene (PTFE). The textural properties and optical behavior of obtained samples were investigated. It was found that after a subsequent heat-treatment in air at 1400°C a strong blue fluorescence of Eu<sup>+2</sup> was observed whereas in thermally sintered samples without fluorination only Eu<sup>+3</sup> ions were present.

## Spectroscopy and crystal field parameters calculations for Ln(III) complexes with 2,2'-bipyridine-1,1'-dioxide (Ln=Pr, Eu)

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The present paper is a continuation of our earlier studies on excited state dynamic of high symmetric [Ln(2,2'-bipyridine-1,1'-dioxide)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> systems [1,2]. It was shown that all RE ions form, with the title ligand (bpyO<sub>2</sub>), complexes of formula [Ln(bpyO<sub>2</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> and are eight coordinated by oxygen atoms of the bpyO<sub>2</sub> molecules. The compound crystallizes depending on the ionic radius of lanthanide ion; Pr(III) and Eu(III) in monoclinic system (P2<sub>1</sub>/c and a = 14.57(1), b = 13.57(1), c = 22.80(10) , β = 92.00(7)°, P2<sub>1</sub> and a = 14.730(1), b = 13.585(1), c = 22.967(2) , β = 91.46(1), respectively) with approximate metal ion D<sub>2</sub> (or lower) symmetry for metal ion center.

The crystal field parameters for Eu(III) were calculated from the experimental set of Stark components of high resolution emission spectra recorded at 77 K in the range of <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>J</sub> (J = 0-6) transitions; the other starting parameters used in calculations were taken from available earlier reported data for related systems [3]. Good correlation was found between experimental and fitted energy levels.

Electronic absorption spectra of [Pr(2,2'-bipyridine-1,1'-dioxide)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub> in solid state and in acetonitrile solution were measured in the spectral range from 400 to 2000 nm. The probabilities of f-f transitions and Judd-Ofelt parameters are analysed in the frame of intensity polarizability mechanism and compared to other high symmetry systems.

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## **Emission studies of submicron silica spheres doped with $\text{Eu}^{3+}$ ions obtained by sol-gel method**

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Sol-gel synthesis of silica spheres with 500 nm diameter is described. Their morphology was studied by transmission electron microscopy at the successive stages of sintering (up to 800 °C). The optical behaviour of silica spheres doped with  $\text{Eu}^{3+}$  ions was investigated. It has been found that size of the spheres does not depend on the sintering temperature. However, emission yield of  $\text{Eu}^{3+}$  increases with the sintering temperature. It is concluded that the increase of emission lifetimes is due to the removing of hydroxyl groups from the surface of silica particles.

**High pressure effect on fluorescence spectra and fluorescence lifetime for  ${}^2E \rightarrow {}^4A_2$  transition in  $\text{LaMgAl}_{11}\text{O}_{19}:\text{Cr}^{3+}, \text{Nd}^{3+}$  and energy transfer between  $\text{Cr}^{3+}$  and  $\text{Nd}^{3+}$**

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For the first time the effect of hydrostatic pressure at the room temperature emission spectra and fluorescence lifetime for  $\text{LaMgAl}_{11}\text{O}_{19}:\text{Cr}^{3+}, \text{Nd}^{3+}$  crystals up to 10 GPa were carried out by DAC. From the position of the R1 peak ( ${}^2E \rightarrow {}^4A_2$  transition) in the emission spectra we estimated the pressure induced red-shift. A dramatic change of the fluorescence lifetime for transition  ${}^2E \rightarrow {}^4A_2$  was observed. The pressure induced lifetime change is described by a simple model. In the considered pressure range (0–10 GPa) good agreement between measured and theoretically predicted values was obtained.

### Blue fluorescence of LaGaO<sub>3</sub>/SrTiO<sub>3</sub> mixed crystals

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A series of La<sub>1-x</sub>Sr<sub>x</sub>Ga<sub>1-x</sub>Ti<sub>x</sub>O<sub>3</sub> solid solution single crystals with  $x = 0, 0.04, 0.08$  and  $0.12$  were grown by the Czochralski method with  $x = 0.01$ , by the floating zone method. The crystals were grown from the melt with stoichiometric Ga<sub>2</sub>O<sub>3</sub> amount at a growth rate ranging from 2.5mm/h for pure LaGaO<sub>3</sub> to 1.2mm/h for  $x = 0.08$ . Large good quality single crystals were grown by the Czochralski method in the concentration range from 0 to 0.04. Thermal analysis proved that the temperature of the first order phase transition observed in pure LaGaO<sub>3</sub> at 150 °C falls to 76 °C at  $x = 0.04$  and remains almost constant at higher  $x$ .

In the absorption spectrum of the crystal there was stated the presence of Ti<sup>3+</sup> ions at octahedral Ga positions in strong crystal field. Ti<sup>3+</sup> ions arise due to some reducing conditions of the crystal growth. It was found that electron delocalization at higher temperature, eg. in oxidation-reduction reaction:  $Ti^{4+} + e = Ti^{3+}$  may appear in optical spectra as charge transfer bands in the NIR region giving rise to blue absorption. The observed fluorescence of <sup>2</sup>E – <sup>2</sup>T<sub>2</sub> transition of Ti<sup>3+</sup> in the crystals shows two bands centered at about 420 and 447 nm coming from excitation at 314, 340 and 384 nm. The fluorescence spectra are strongly polarized.

The goal of the present work is to examine growth conditions, optical spectra and potential emission characteristics of Ti doped LaGaO<sub>3</sub>/SrTiO<sub>3</sub> mixed crystal, which may be of interest for practical laser application. We analyze also the influence of annealing in oxidizing and reducing atmospheres and  $\gamma$ -irradiation treatments on optical properties of Ti doped LaGaO<sub>3</sub>/SrTiO<sub>3</sub> mixed crystals.

## High-pressure spectroscopy of $\text{Cr}^{3+}$ doped nonstoichiometric green spinel $\text{MgO-2.5Al}_2\text{O}_3$

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The discovery of room temperature laser operation for  $\text{Cr}^{3+}$  in low crystal fields has directed attention towards the  $\text{Cr}^{3+}$ -doped materials exhibiting a broadband luminescence appropriate for tunable solid state laser. The  $\text{Cr}^{3+}$ -doped  $\text{MgO-2.5Al}_2\text{O}_3$  non-stoichiometric synthetic spinel exhibits a strong luminescence band in the near infrared spectral region, characteristic for the  $\text{Cr}^{3+}$  ions in a low crystal field environment.

Optical properties of synthetic spinels are not well understood yet. It is known, that these synthetic crystals exhibit large disorder in comparison with natural spinels. Chromium ions in spinel crystals have been found to occupy several sites of various symmetries. However different authors have found different number of this sites – from 2 to 25 [1 – 6].

We used a diamond-anvil cell high-pressure technique at low temperatures to study the spectroscopic properties of  $\text{Cr}^{3+}$  ions in  $\text{MgO-2.5Al}_2\text{O}_3$  crystal. Application of high-pressure reduces the distances between a dopant ion and the ligands. Thus it increases the strength of the crystal field experienced by the dopant centers. Due to increase of the strength the broadband, shortlived luminescence from the  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transition is gradually replaced with sharp line, longlived luminescence from the  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  transition. This improves considerably spectroscopic resolution of measurements and allows to obtain information on the multicenter structure of dopants.

The results of high-pressure studies of non-stoichiometric synthetic  $\text{Cr}^{3+}$ -doped  $\text{MgO-2.5Al}_2\text{O}_3$  spinel are reported in this paper. The pressure dependence of the luminescence and their decay kinetics has been studied. The results reveal new information about the electronic structure of different  $\text{Cr}^{3+}$  centers in this crystal. There are five major  $\text{Cr}^{3+}$  centers in this crystal. These centers correspond to  $\text{Cr}^{3+}$  ions in the sites with different crystal-field. At ambient pressure four of these centers experience strong crystal-field and one of them is the intermediate crystal-field center. Two of the strong crystal-field centers and the intermediate crystal-field center exhibit enormous inhomogeneous broadening, up to  $500\text{ cm}^{-1}$ . This is probably the reason, why all the broad luminescence of this spinel was regarded up to now as originating from the low crystal-field chromium centers.

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## Application of lanthanide (Eu, Nd) spectroscopy as a structural probe of double phosphates

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Lanthanide phosphates are the subject of wide investigations which are motivated by their important physical properties, and especially their application in laser devices.

Double phosphates crystallize mainly in two phases: hexagonal and ortho-rhombic, and some modifications of them (monoclinic) depending on the lanthanide ionic radius and kinds of M(I) ions. The present studies are focused on the application of europium(III) emission as a structural probe of diluted double phosphate; determination of the number of sites, as well as their symmetries. The influence of the M(I) ions on the structure of phosphates is shown in the emission spectra at 77 K. The IR and Raman spectra were measured and used in assignment of the vibronic components of electronic transitions. The electron-phonon coupling was analyzed in emission and excitation spectra of europium double phosphate.

Moreover, absorption spectra at 293 and 4K as well as intensity analysis of Nd(III) f-f transition were used in detection of structure modifications in both the types of phosphates: rubidium (1) and sodium (2) salts. The energy level diagram was proposed and compared to the earlier reported data for different types of phosphates.

Since the strongest vibronic coupling is expected for Yb(III) phosphate, both the absorption and resonance emission spectra were analyzed and related to the IR and Raman data. The effort was made to elucidate the cooperative effect in Yb(III) absorption and emission spectra.



## High resolution spectroscopy of $R_2BaMO_5$ ( $R$ =Rare Earth $M$ =Cu, Zn, Co)

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The compounds with the same formula,  $R_2BaCuO_5$ , are well known to crystallise in different symmetry space groups. One of them, the orthorhombic  $Pnma$  group, comprises a great amount of compounds. We have investigated several of them, namely  $Er_2BaMO_5$  with  $M$ =Cu, Zn, Co, and  $R_2BaCuO_5:Er(1\%)$  with  $R$ =Dy, Ho by means of high-resolution Fourier-transform spectroscopy. Comparison of crystal field levels of the  $Er^{3+}$  in these compounds reveals a close similarity of crystal field. Nevertheless, their magnetic behaviour, according to our spectroscopic data, is different. For  $Er_2BaZnO_5$  we failed to detect any magnetic interactions down to the temperature of 2K. This means that the exchange interaction between the rare earth ions (R-R) is extremely small. The fine structure of the spectral lines in  $Er_2BaZnO_5$  has been attributed to the Davydov (factor-group) splitting. Very different magnetic behaviour of the compounds with  $M$ =Cu means that the exchange interaction between copper and rare earth (R-Cu) is of great importance. The R-Co interactions are much smaller, as it follows from our spectral data on  $Er_2BaCoO_5$ . Detailed analysis of the magnetic interactions in  $Dy_2BaCuO_5$  and  $Ho_2BaCuO_5$  has shown that the anisotropic Dzyaloshinskii-Moria interaction is a dominant one at low temperatures.

Another compound investigated,  $Nd_2BaCuO_5$ , belongs to the  $P4/mbm$  tetragonal space group. Comparison of our spectroscopic data with those on  $Nd_2BaZnO_5$  gives a close similarity of the crystal fields in these compounds although the space group for Zn-compound is another one ( $I4/mcm$ ). We explain this result by peculiarities of the two structures. Temperature dependencies of the Kramers doublet splittings can be explained only assuming quasi-one-dimensional magnetic interactions. Analysis of the structure and magnetic moments carried out on the basis of neutron diffraction data confirms this assumption.

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## Features of spectroscopy and formation process of the sol-gel films doped with silver nanoparticles

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Metal and semiconductor nanoparticles are studied intensively last years as unique species for spectroscopy in the broad range of wavelengths: fundamental absorption, excitation of collective resonance states, intraband electronic transitions, etc. provide efficient pathways of interaction with light radiation manageable by a number of particle properties. Besides the chemical nature of nanoparticles, their size, surface states, particle-matrix interactions are the means for regulation of spectroscopic parameters of the nanoparticle-containing systems. Silver nanoparticles in this field are rather popular subject due to the familiar plasmon resonance in the near UV/visible, however, a lot of open questions remains up to date since there is a diversity of factors influencing optics of silver. It is worthwhile to develop a medium for study of silver particle optics covering the wide size range of them and preventing the chemical effects those could vary the surface of silver nanoparticles. Moreover, the problem of successful stabilization of nanoparticles and clusters of silver is also of essential importance; liquid- and gaseous phase methods of the silver particles production do not satisfy these requirements. In the present work, we develop the fabrication of solid materials in the form of thin silica-based films containing silver nanoparticles and show some pathways to control their size and spectral features. A sol-gel technique is one of most useful methods for preparation of similar films due to possibility of preparation condition changes at different steps.

Silver nanoparticles were produced within the silica sol-gel films by introduction of silver salts into precursor sol (up to 5 wt.%). The liquid precursors were deposited onto quartz substrates by spin-coating. A gelation followed by drying next occurred resulting in the formation of thin (typically 0.1–0.5  $\mu\text{m}$ ) films. Several compositions of the sols change their acidity, viscosity, and porosity of the final films. These factors appeared to be crucial for optical features observed for silver particles incorporated.

The films were heat treated in air and exposed in reduction atmosphere (hydrogen). Different temperatures of the heat treatment and reduction lead to the variable spectral position of the silver plasmon resonance, its spectral width, and stability with respect to subsequent oxidation under heating in air. It was remarkable an unambiguous observation of a new optical feature ( $\lambda_{\text{max}} = 320\text{--}350\text{ nm}$ ), which scarcely could be assigned to the silver plasmon resonance, under mild reduction conditions ( $t = 100\text{--}150^\circ\text{C}$ ), and the whole spectrum had a two-peak shape. Such short-wavelength maximum can be attributed to few-atomic silver clusters according to previous studies of them in colloids, frozen rare gases and zeolites. An increase of silver concentration in the films resulted in flattening of the two-peak structure, and the broad maximum at  $\lambda > 400\text{ nm}$  was developed.

The two types of spectroscopic manifestation of silver in the sol-gel silica films can be associated with complicated nanoporous structure of the latter: two or more pore dimensions under appropriate conditions are to stabilize different size ranges of silver particles (clusters,  $< 1\text{ nm}$ , and  $1\text{--}100\text{ nm}$  diameter).

## Photoluminescence investigation of porous anodic alumina with spin-on europium-containing titania sol-gel films

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Europium is widely used as a dopant for fabrication of phosphors for red light emission. Red photoluminescence (PL) from  $\text{Eu}^{3+}$  ions originates from  $\text{D} \rightarrow \text{F}$  electron transitions resulting in sharp peak at 617 nm. Different methods are used for fabrication of the lanthanide-doped materials such as ion implantation, electrochemical deposition, sputtering in vacuum, sol-gel synthesis, etc. In this work, we investigate europium-containing sol-gel derived films fabricated onto porous anodic alumina of 30  $\mu\text{m}$  thick and pore diameter of 100 nm. The sols were prepared from  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  precursor mixed with aqueous-alcohol solution of europium nitrate. Concentration of europium oxide in xerogel was 40 wt.%. Spin-on procedure at 2700 rpm followed by drying at 473 K at ambient atmosphere was used to fabricate the luminescent Eu-doped films. Multilayered coatings were obtained by sequential spin-on deposition followed by drying. Investigation of excitation spectra showed that the maximum PL intensity was observed at excitation wavelength of 285 nm. The PL spectra have typical for  $\text{Eu}^{3+}$  bands corresponding to  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $j=1\dots4$ ) electron transitions with the maximum at 617 nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ). Increase of spin-on depositions from 1 to 10 lead to decrease of PL intensity. Decrease of PL temperature from 300 to 10 K results in about 5-time increase of PL intensity. The half-width of the main band at 617 nm is about 25 nm at room temperature.

## Visible luminescence from europium-doped alumina sol-gel- derived films confined in porous anodic alumina

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In this work, the results on photoluminescence (PL) investigations of europium-doped alumina sol-gel-derived films on porous anodic alumina are presented. Sol-gel method of fabricating the lanthanide-doped films is attractive due to its low cost and fabrication of the thermodynamically stable products. Use of porous anodic alumina with a regular pore morphology as a template for xerogel deposition allows creation of materials with tunable optical properties and strong PL [1-3]. Moreover, such materials have higher chemical and temperature stability in comparison to organic dyes-containing ones. PL from europium containing alumina xerogels deposited onto porous anodic alumina with pore depth and diameter of 30  $\mu\text{m}$  and 100 nm, respectively, was investigated at excitation wavelength of 300 nm. The PL spectra represent a typical for  $\text{Eu}^{3+}$  ions set of peaks with the maximum at 617 nm. PL intensity was found to increase with increase of Eu content in xerogel. Cooling the samples from 300 to 10 K leads to increase of PL intensity. Eu PL increases nearly linearly with the excitation power within a range up to 25 mW/cm<sup>2</sup>. Red Eu-related PL from all of the samples is visible to a naked eye even at room temperature. Thus, we propose to consider the Eu-doped xerogels onto porous anodic alumina as a basis for fabrication of thin-film luminescent images.

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## Valency change of regular and doped nl-ions and radiation defects in solids

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In our talk have to make the analysis of separate experimental data and results of the *ab initio* calculations of spectroscopic characteristics of simple and complex oxide single crystals doped by Me- and/or RE-ions before and after irradiation and thermal treatment. We have studied that during irradiation or thermal treatment colour, impurity and radiation defects of the perfect and non-stoichiometry AO,  $A_2O_3$ ,  $ABO_3$ ,  $A_3B_2C_3O_{12}$  single crystals have to formate and transform. Change of electronic states of regular and doped ions during influence were studied in detail. Change of the valency of the separate part of regular and doped Me-ions leads to arise of the structural defects at the nearest encirclement and local electronic levels in forbidden zone. Change of the electronic state of regular and doped ions leads to change of the electrical, optical and others characteristics of the solids [1-5]. Relation of the valency, parameters of the electronic structure of the doped ions and spectroscopic properties of the pure and doped crystals was investigated carefully.

Anomaly of the separate properties of the pure and doped oxide single crystals [6-8] were studied in the framework of approach for change of Madelung's constant, stoichiometry and change of the valency of impurities and regular ions.

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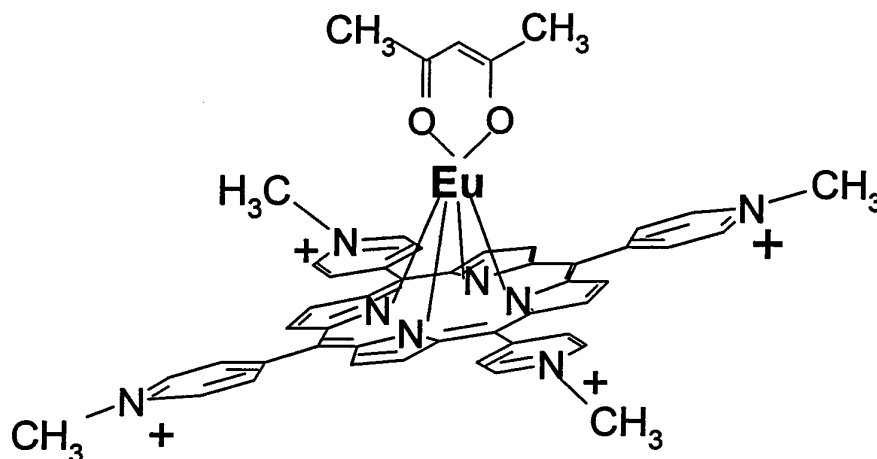
## Spectroscopic properties of the water-soluble cationic porphyrins and their complexes with Cu(II) and Eu(III), encapsulated in the silica matrices prepared by sol-gel method

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Porphyrins are known to play a significant role in several biological systems. For example, the presence of such complexes is essential for the activation and storage of oxygen (hemoglobin and myoglobin), electron transfer (cytochrome c, cytochrome oxidase) and solar energy transfer (chlorophyll). Porphyrins are versatile molecules whose physicochemical properties can be readily adjusted by modifications of the electronic distribution on the aromatic ring via peripheral substitution.



**EuTMePyP(acac)**

Europium(III) acetylacetonate 5,10,15,20-tetrakis (1-methyl-4-pyridyl) porphine

The sol-gel process allows the insertion of organic molecules in inorganic or hybrid (organic/inorganic) matrices. A large variety of new glass-like doped materials can be processed and finalized for applications as optical or electronic devices. The great advantage of the sol-gel method is possibility of the encapsulation organic dyes, such as porphyrins in an inorganic network. Silica matrices doped with dyes have many applications in catalysis, non-linear optics and can serve as probes to investigate pH, metal ions etc.

The silica gel matrices doped with water-soluble porphyrins: H<sub>2</sub>TTMePP {tetrakis [4-(trimethylammonio)phenyl]}, H<sub>2</sub>TMePyP [tetrakis(1-methyl-4-pyridyl)] and their complexes with copper (II) and europium (III) were prepared. We investigated their absorption and emission spectroscopic properties in solutions, silica gels and solid-state. The spectra of metal complexes were compared with those of free-base porphyrins.

**Excited state dynamics of Nd<sup>3+</sup> ions in highly concentrated Nd:YAG ceramics**

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**Comparison of the spectroscopic data of  $\text{Tm}^{3+}$  ions in the different hosts:  
 $\text{KLn}(\text{MoO}_4)_2$  where  $\text{Ln} = \text{Y, La and Lu}$**

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Polarized infrared and Raman scattering spectra of potassium rare-earth double molybdates ( $\text{KLn}_x\text{Tm}_{1-x}(\text{MoO}_4)_2$ , where  $\text{Ln} = \text{La, Y, Lu}$ ) were measured in the range of  $40 - 1000 \text{ cm}^{-1}$  at ambient temperature. The distribution of vibrational levels was related to the results of unit-cell modes. Factor group analysis was performed to determine the symmetries and nature of the observed modes. The crystal structure of the compounds studied depends on the type of cation and changes from tetragonal to orthorhombic. The character of the coordination sphere around the molybdenum atom changes from tetrahedral to octahedral. The assignment of the observed bands to the respective internal and external vibrational modes is proposed.



**Synthesis, X-ray structure and spectroscopic studies of new praseodymium(III) six-coordinate complexes with 3-halo-4-methoxy-2,6 lutidine-N oxide:  $\text{PrCl}_3(\text{XCH}_3\text{OC}_7\text{H}_7\text{NO})_3$  where X = Cl, Br and I**

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X-ray structure of new  $\text{PrCl}_3(\text{BrCH}_3\text{OC}_7\text{H}_7\text{NO})_3$  compound has been determined and described in monoclinic space group  $\text{P2}_1/\text{n}$  with 4 molecules per unit cell of the dimensions:  $a = 8.232$ ,  $b = 23.733$ ,  $c = 16.763$  Å and  $\beta = 90.75^\circ$ . The  $\text{Pr}^{3+}$  ion is six-coordinated with three  $\text{Cl}^-$  ions and three oxygen ions of the N-oxide group of the bromo-lutidine moieties. The molecules are linked through a medium strong hydrogen bonds of the type  $\text{C-H}\cdots\text{Cl}$  and length 3.591 Å. The chlorine and iodine derivatives of the lutidine N-oxide have also been synthesized and their properties compared to the bromine complex. The FTIR and FT Raman spectra as well as electronic absorption and emission spectra have been recorded and analyzed in terms of site symmetry and energy level scheme of praseodymium(III) ion. The potential application of these materials as a precursor to light-conversion is discussed.

## Absorption and luminescence spectroscopy of the $\text{MnO}_4^-$ centers in alkali halide crystals

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The first low-temperature (4K) absorption, near infrared photoluminescence (NIRPL) and photoluminescence excitation spectra (PLE) of the  $\text{MnO}_4^-$  and  $\text{MnO}_4^{2-}$  doped KI and RbI crystals are reported.

The crystals which contain nominally  $\text{MnO}_4^-$  ions have been obtained as a result of  $\text{MnO}_4^{2-}$  oxidation of the  $\text{MnO}_4^{2-}$ -doped samples by using a special electrolytic coloration procedure. The most intense low-energy bands in the optical absorption spectra observed are centered at about 500nm (in crystals doped with  $\text{MnO}_4^-$  ions) and at about 600nm (in  $\text{MnO}_4^{2-}$  doped crystals). We assign these ligand-to-metal charge transfer (LMCT) bands to  $^1A_1 - ^1T_2$  ( $1t_1-e$ ) and to  $^2E - ^2T_2$  ( $1t_1-e$ ) intramolecular transitions, respectively. At 4K LMCT bands of both ions exhibit the well developed vibrational progressions in the Mn-O stretching mode.

The NIRPL spectra were excited by Ar-laser line 514.5nm and by Kr-laser line 647.1nm via LMCT bands. The broad emission bands were observed in both  $\text{MnO}_4^{2-}$  and  $\text{MnO}_4^-$  doped crystals, practically, in the same spectral region (900-1200 nm). The NIRPL of  $\text{MnO}_4^{2-}$  doped crystals is connected with d-d ( $^2T_2 \rightarrow ^2E$ ) ligand-field transition of the single 3d-electron of the  $\text{Mn}^{6+}$  ion. PLE spectra of the KI: $\text{MnO}_4^{2-}$  and RbI: $\text{MnO}_4^{2-}$  coincide well with observed LMCT absorption bands

In case of the  $\text{MnO}_4^-$  ion the 3d-shell of the manganese is empty and NIRPL band could not be, therefore, ascribed to  $\text{MnO}_4^-$  ion. In fact, a significant difference has been observed between the excitation profile and  $\text{MnO}_4^-$  induced absorption band in crystals doped with the  $\text{MnO}_4^-$  ions.

To explain the NIRPL bands in  $\text{MnO}_4^-$ -doped crystals we have studied the NIRPL intensity temperature dependence in the interval 4–300K. The integral intensity below 100K was found to obey the Arrhenius thermoactivation law:

$$I(T) = I_0 \exp(-U_{ac}/T) + I_1.$$

The thermoactivation energy  $U_{ac}$  was estimated for KI and RbI crystals. The model proposed implies that the temperature increase is followed by trapping of an external electron into the ground 3d-state of  $\text{Mn}^{7+}$  ion causing the transformation of  $\text{MnO}_4^-$  into  $\text{MnO}_4^{2-}$ . In this case the new center symmetry should be assumed to be the same as that for the host  $\text{MnO}_4^-$  ion, i.e.  $T_d$ . This model could explain the occurrence of the NIRPL-band in  $\text{MnO}_4^-$ -doped crystals and the different NIRPL-bandshapes activated by these two types of  $\text{MnO}_4^{2-}$  centers which possess of  $C_{2v}$  and  $T_d$  symmetry, respectively.

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**'Spectroscopic behavior' of  $\text{Yb}^{3+}$  ions in tellurite-tungstate glasses**

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It is accepted to consider [1] that ytterbium is characterized by the most coordinating stability of all rare earth elements and its 4f-electrons participate in chemical bond with ligands in the least degree. For an elucidation of the situation, we investigated the absorption and electron paramagnetic resonance spectra of the activator in glass of  $\text{TeO}_2\text{-WO}_3\text{-Yb}_2\text{O}_3\text{-K}_2\text{O}$  system. It is established that with increase of  $\text{K}_2\text{O}$  concentration from 0 to 25 mol.% the barycenter of  $^2\text{F}_{7/2}(1) \leftrightarrow ^2\text{F}_{5/2}(1)$  band at  $T = 4.2$  K displace to short-wavelength band of spectrum up to  $15\text{ cm}^{-1}$ , the half-width of the band increase from  $60\text{ cm}^{-1}$  to  $85\text{ cm}^{-1}$  and the probability of optical transition decrease up two times both in resonance and in nonresonance channels. Moreover, at concentration of  $\text{K}_2\text{O} \geq 15$  mol.%, the 'superfluous' stark component for the band of  $^2\text{F}_{7/2} \leftrightarrow ^2\text{F}_{5/2}$  is appeared. In EPR-spectrum of alkali free glass at  $T = 19$  K, the weak signal at  $g \approx 2.0$  connected with  $[\text{YbO}_6]$  polyhedrons is observed. As the alkali concentration is increased, the signal is decreased and an intensive signal at  $g \approx 4.7$  is appeared. The results testifies to low coordinating stability of  $\text{Yb}^{3+}$  ions in the glasses and participation of the activator 4f-electrons in chemical bond with ligands.

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## Modelling of light generation in microdisk Nd:YAG lasers

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Microdisk waveguides, resonators, and lasers are important optoelectronic devices because of the possibility of their implementation as compact and efficient passive or active devices, based on their high Q circular structure. Particularly microdisk lasers have low threshold and the low-order transverse-electric (TE) mode are dominant. Experimental results also revealed a possibility of a narrow-band single-mode lasing and a high spontaneous emission coupling strength [1].

The design and optimisation of microdisk lasers is critically dependent on the Q factor of the resonant optical modes, as well as on the spectral and spatial overlap of these mode with the active medium. Moreover, in order to optimised power efficiency of the laser one also needs to take into account gain saturation effect. In most of the theoretical descriptions of this kind of lasers, 2-D or 3-D mode analysis (based on the confocal transformation) were performed and the spontaneous emission coupling factor was analysed [1].

In this paper we present a systematic study of the nonlinear operation of microdisk Nd:YAG lasers. In our approach we have started from vector-wave self-consistent mode equations taking into account three-dimensional spatial field dependence of laser modes. First we solve the threshold conditions, obtaining threshold gain and spectrum for whispering-gallery modes (having large azimuthal mode index) and for radial modes (having low azimuthal mode index). Next we include gain saturation effect. On the basis of the energy conservation theorem [2] we derive an approximate formula which relates the small signal gain in the Nd:YAG active medium to the output power and real parameters of the laser structure. In particular, the laser characteristics, obtained for whispering-gallery modes and radial modes, reveal the behaviour of the optimal outcoupling coefficient (which provides maximal power efficiency) as a function of the structure parameters.

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## Nanosized glass ceramics doped with transition metal ions: nonlinear spectroscopy and possible laser applications

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Technological boom during recent decades is caused in many aspects by new materials appeared. Among them transparent glass ceramics have had a wide spectrum of applications valued primarily for their near-zero thermal expansion and high thermal stability: high precision optics, stove cooktops, fire doors, etc. Another possible range of transparent glass ceramics applications is related with the possibility to dope this material with transition metal or rear-earth ions. Such applications include solar collectors, upconversion devices, laser active and passive media.

This paper presents study of linear and nonlinear optical properties of magnesium-aluminum glass ceramics doped with  $\text{Co}^{2+}$  ions (Co:MAS). Influence of heat treatment conditions on optical properties of this transparent glass ceramics is analysed in comparison with the properties of  $\text{Co}^{2+}$ -doped magnesium-aluminum spinel single crystal.

The absorption spectra of Co:MAS samples with intensive bands in visible and near infrared are formed in the material heat treated at 800-1000 °C after the first hold at 750 °C. The spectra are characteristic for pure tetrahedrally co-ordinated  $\text{Co}^{2+}$ , which is clearly seen from comparison with the absorption spectrum for  $\text{Co}^{2+}:\text{MgAl}_2\text{O}_4$  single crystal (Co:MALO). Our study showed that (i) increasing the amount of CoO in the raw material; (ii) rising the temperature of the second stage treatment; (iii) prolonging the duration of the second stage treatment cause increase the amount of tetrahedrally coordinated  $\text{Co}^{2+}$  ions in the magnesium-aluminum spinel nanocrystals due to ions entering into the nanocrystals from glass surrounding.

The sample after two-stage heat treatment demonstrates luminescence signal at least 100 times higher in intensity than before treatment. Shape of the luminescence spectrum and intensity ratio between the bands are similar to that ones for Co:MALO – with intense band at 680 (or 690 nm) and less intense band centered at 935 nm. For  $\text{Co}^{2+}:\text{MgAl}_2\text{O}_4$  crystal luminescence bands at 660 nm and 880 nm correspond to the transitions  ${}^4\text{T}_1({}^4\text{P}) \rightarrow {}^2\text{A}_2$ ,  ${}^4\text{T}_2$ , respectively. We attribute the luminescence bands for heat-treated Co:MAS samples to the same transitions as for Co:MALO spinel crystal. For all the samples decay of luminescence signal is not monoexponential. We estimated the characteristics times of the luminescence decay as the time of decrease to 1/e level and obtained values of 40, 32 and 25 ns for Co:MAS samples with weight content of CoO in the raw material of 0.1, 0.3 and 0.5%, respectively.

The bleaching relaxation time of the Co:MAS samples under excitation of  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1({}^4\text{F})$  transition and the absorption saturation at 1.54  $\mu\text{m}$  were measured. The bleaching decay was mono exponential for the both 0.1 wt% and 0.3 wt% Co:MAS samples with a time constant  $\tau \approx (450 \pm 150)$  ns and  $(120 \pm 40)$  ns, respectively. The absorption saturation measurements showed that Co:MAS samples demonstrated different values of nonsaturable losses  $\alpha_{ns}$  under various CoO content in the material. The values of  $\alpha_{ns}$  were estimated of 0.7 and 1.9  $\text{cm}^{-1}$  for 0.1 wt% and 0.3 wt% Co:MAS samples at 1.54  $\mu\text{m}$ , respectively. The best fit to the experimental data were obtained with the values of  $\sigma_{\text{GSA}} = 3.3 \times 10^{-19} \text{ cm}^2$  for 0.1 wt% Co:MAS samples and  $\sigma_{\text{GSA}} = 3.9 \times 10^{-19} \text{ cm}^2$  for 0.3 wt% Co:MAS samples at 1.54  $\mu\text{m}$ . These values are close to the value of  $\sigma_{\text{GSA}} = (2.8 \pm 0.4) \times 10^{-19} \text{ cm}^2$  measured for the  $\text{Co}^{2+}:\text{MgAl}_2\text{O}_4$  single crystal.

## VUV luminescence of $\text{LiYF}_4\text{:Er}$ and $\text{BaY}_2\text{F}_8\text{:Er}$ crystals under inner-shell excitation

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The interconfigurational  $4f^{n-1}5d-4f^n$  transitions of rare earth ions have been extensively studied, due to their potential application as scintillator materials and active media for the VUV lasers. The VUV emissions of heavier lanthanides in fluoride hosts have been investigated at the SUPERLUMI station of HASYLAB at DESY using photons up to 40 eV. As it was shown earlier, the  $d-f$  emissions in  $\text{LiYF}_4\text{:Er}$  and  $\text{BaY}_2\text{F}_8\text{:Er}$  are effectively excited by photons in the energy range of  $f-d$  absorption, while exciting efficiencies in host absorption emission are very low [1–3]. In this report we focus our attention on the luminescence of  $\text{Er}^{3+}$  in same crystals, but the studies were performed under soft X-ray excitation.

The measurements were carried out at the BW3 beamline of HASYLAB at DESY under excitation by synchrotron radiation from the DORIS storage ring. The decay kinetics, time resolved emission and excitation spectra of  $\text{LiYF}_4\text{:Er}$  and  $\text{BaY}_2\text{F}_8\text{:Er}$  crystals in the temperature range from 10 to 300 K were recorded using a 0.4 m monochromator in Seya mounting equipped with a microchannel-plate detector (FWHM  $\sim 300$  ps). The energy range of excitation was 40–200 eV.

The excitation efficiency of both the fast (155 nm) due to spin-allowed (S-A) transitions and slow luminescence (163 nm) due to spin-forbidden (S-F) transitions in  $\text{LiYF}_4\text{:Er}$  increases continuously with the excitation energy, being modulated by inner-shell absorption (e.g.  $1s \text{ Li} \sim 60$  eV). A strong concentration quenching is observed in the decay of the  $\text{Er}^{3+}$  S-A emission. The lifetime shortens from 2.96 ns to 1.95 ns for samples with 3 and 30 % concentration of  $\text{Er}^{3+}$ , respectively. Although, a higher content leads to the decrease of the total emission intensity, the intensity of the S-A component increases with respect to that of the S-F emission.

A new weak emission band at 150 nm, above the well-known S-A transition (160 nm), was revealed in  $\text{BaY}_2\text{F}_8\text{:Er}$  (5%) crystal at 10 K. The decay of this emission is faster than that of the S-A transition and lies in the sub-nanosecond range. It is thermally quenched at 90 K. The origin of this emission is not clarified yet, but some possibilities, like emission from higher  $d$ -states or from the  $d$ -states of  $\text{Er}^{3+}$  ions situated in sites with symmetry other than trigonal, will be discussed.

Luminescence properties of  $\text{Er}^{3+}$  ions under soft X-ray excitation will be compared with those, obtained under direct photoexcitation of  $d$ -shell.

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## Sol-gel processed $\text{Eu}^{2+}$ doped alkaline earth aluminates, $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$ ( $\text{M} = \text{Ca}, \text{Sr}$ )

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$\text{Eu}^{2+}$  doped alkaline earth aluminates  $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$  ( $\text{M} = \text{Ca}, \text{Sr}$ ) show strong luminescence at the blue/green region [1]. The luminescence is characterized by a rapid initial decay from  $\text{Eu}^{2+}$  followed by very long afterglow. The afterglow enhanced by co-doping with some  $\text{RE}^{3+}$ -ions, may be due to the thermal activation of holes from traps followed by the emission of  $\text{Eu}^{2+}$  [2]. The detailed mechanism is not, however, understood.

The sol-gel process is an efficient technique for the preparation of phosphors due to the good mixing of starting materials and relatively low reaction temperature. The solid state preparation of  $\text{MA}_2\text{O}_4$  is usually carried out at around  $1300^\circ\text{C}$  since impurities as  $\text{M}_3\text{Al}_2\text{O}_6$  are formed at lower temperatures. With the sol-gel technique, a lower temperature ( $900^\circ\text{C}$ ) is reported for the successful preparation of  $\text{MA}_2\text{O}_4$  ceramics [3].

In this work, the  $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$  phosphors were prepared by the sol-gel method. Thermal analysis revealed that the sol-gel technique lowered the reaction threshold temperature with  $300^\circ\text{C}$  compared to the solid state reaction. However, by-products were observed in the X-ray diffraction pattern if the final heating temperature was below  $1200^\circ\text{C}$ . The metastable, presumably hexagonal phase of  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$ , not formed in the solid state reaction, was obtained by the sol-gel technique at  $850^\circ\text{C}$ . The structure of this phase was studied.

The luminescence of the sol-gel products was observed at the same region as the solid state prepared materials but the band of metastable  $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$  was observed at slightly higher wavelength than the normal monoclinic phase. Thermoluminescence was also studied and compared to solid state prepared  $\text{MA}_2\text{O}_4:\text{Eu}^{2+}$ . Persistent luminescence mechanisms were proposed based on the results of the presented experimental work.

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## X-ray and spectroscopic characteristics of a new class of mixed lanthanide chelates of the type $\text{LnWo}_3 \cdot \text{Ph}$ ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{Tb}$ )

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Lanthanide  $\beta$ -diketonates of formula  $\text{Ln}\beta_3\text{L}$  (L is another ligand) have wide applications as NMR shift reagents and luminescence labels in fluoroimmunoassays. In the sixties these compounds were the first used for laser action in liquid phase and in the nineties - as electroluminescence diodes [1, 2]. On the other hand, the phosphoro-azo derivatives of  $\beta$ -diketonates were used as anticancer agents [3]. The knowledge about the lanthanide complexes is not sufficient. Recently we have published X-ray and spectroscopic investigations for three types of their lanthanide chelates [4–6].

The aim of this paper are the spectroscopic studies and results of X-ray diffraction of the new class of mixed lanthanide compounds of the type  $\text{LnWo}_3 \cdot \text{Ph}$  (where:  $\text{Wo} = \text{CCl}_3\text{--C(O)--N--P(O)--(OCH}_3)_2$ ;  $\text{Ph} = 1,10\text{-phenantroline}$ ,  $\text{Ln} = \text{Sm}, \text{Eu}, \text{Tb}$ ). The absorption, emission and excitation spectra at room and low (77 K) temperatures of the title monocrystals were measured. Analysis of f-f transition was made and the oscillator strength values for samarium and terbium complexes were compared to those for  $\text{Na}[\text{LnWo}_4]\text{H}_2\text{O}$  [4]. Luminescence spectra at 77 K for the Eu analogue are very complicated and point that  $\text{Eu}^{3+}$  ions reside in the structure at two low symmetry sites. It manifests in splitting of the respective levels. Analysis of emission spectra for terbium complex confirms the data for europium title crystals. Spectroscopic results correspond well to crystal structure of the mixed  $\text{SmWo}_3 \cdot \text{Ph}$  compound and confirm isostructural the monocrystals containing  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ .  $\text{SmWo}_3 \cdot \text{Ph}$  crystallises in a monoclinic space group  $\text{P2}_1/\text{c}$  with unit cell parameters:  $a = 19.480(2) \text{ \AA}$ ,  $b = 21.875(2) \text{ \AA}$ ,  $c = 21.415(3) \text{ \AA}$ ,  $\beta = 109.459(8)^\circ$ . There are two different  $\text{Sm}^{3+}$  ions with insignificant difference between  $\text{Sm--O,N}$  bonds ( $0.005 \text{ \AA}$ ) and  $\text{C. N.} = 8$ . Comparison of  $\text{EuWo}_3 \cdot \text{Ph}$  and  $\text{TbWo}_3 \cdot \text{Ph}$  excitation spectra clearly points location of the C-T band. Strong vibronic coupling with ligand internal vibrations was observed mainly with  ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$  electronic transition. The IR spectra were used to analyse the vibronic components.

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## Crystal structure, magnetism and photophysics of lanthanide (Nd, Sm) maleates

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Lanthanide carboxylates are the subject of the several recent studies because of their applications. Usually lanthanide carboxylates create dimeric and polymeric networks in the crystal structure. Recently we reported the results of the X-ray diffraction and spectroscopic studies of a series of lanthanide polynuclear and heteronuclear carboxylates [1–4]. The present work describes the crystal structure of two lanthanide maleates. Electronic spectroscopy, IR, Raman and magnetic measurements were used to characterise the title compounds.

X-ray diffraction studies were done for neodymium single crystal of  $\text{Nd}(\text{C}_4\text{O}_4\text{H}_3)_3 \cdot 8\text{H}_2\text{O}$ . The crystal structure is triclinic ( $P-1$ ,  $Z = 2$ ,  $a = 7.285(1) \text{ \AA}$ ,  $b = 10.394(2) \text{ \AA}$ ,  $c = 16.765(3) \text{ \AA}$ ,  $\alpha = 72.13(2)^\circ$ ,  $\beta = 87.77(2)^\circ$ ,  $\gamma = 70.86(2)^\circ$ ,  $R_{\text{all}} = 0.0322$ ) and isotypic with the respective praseodymium compound [5]. The  $\text{Nd}^{3+}$  ion creates nine-fold coordination polyhedra. Two carboxyl groups for two independent maleic groups are involved in metal ion coordination in a monodentate manner. The third maleic anion forms hydrogen bonding with unbounded water and coordinated water molecules. Moreover, there is very strong intramolecular hydrogen bonding ( $\approx 2.45 \text{ \AA}$ ) in all maleic ions. Since  $\text{C}=\text{C}$  double bond increases rigidity of the ligand anion, creation of 7-membered rings by two carboxyl groups becomes unavailable.

Absorption spectra of neodymium and samarium single crystals at 293 and 4.2 K were measured. Analysis of the f-f transition probabilities were performed and Judd-Ofelt parameters were determined. Strong vibronic coupling was found, mainly promoted by modes which correspond to coordinated moieties of ligand molecules. Since X-ray data points on one symmetry site of the  $\text{Nd}^{3+}$  ion, a structural transformation is expected basing on split  $^4\text{I}_{9/2} \rightarrow ^2\text{P}_{1/2}$  transition in the spectra at 4.2 K. It can find confirmation in relatively high temperature factors in X-ray data. Magnetic susceptibility results were correlated with X-ray data and our earlier reported results of dimeric systems [3–4].

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## Multiphonon relaxation of the mid IR transitions of rare-earth ions in the crystals with fluorite structure

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To find regularities of the multiphonon relaxation (MR) rates in the pair optical centers of rare-earth ions on the number of phonons  $n$  participating in the process, on the cation mass and  $a$  parameter of the crystal lattice the kinetics of fluorescence decay of the  $^4I_{9/2}$  state of erbium was measured at 77K under direct laser excitation in the  $\text{CaF}_2$ ,  $\text{CdF}_2$ ,  $\text{SrF}_2$ ,  $\text{PbF}_2$  and  $\text{BaF}_2$  crystals and in crystals codoped with  $\text{Y}^{3+}$ ,  $\text{Lu}^{3+}$  or  $\text{Yb}^{3+}$ . The equation for the phonon factor of crystal matrix  $\eta$  depending on the cation mass, the crystal unit dimension (the  $a$  parameter) and maximum phonon frequency  $\omega_{\max}$  of crystal lattice is derived. A single frequency approach of the spectral phonon density of states of crystal lattice was used. A decrease of the phonon factor  $\eta$  with increase of a crystal lattice parameter  $a$  and a cation atom mass is directly followed from this equation. This in its turn tends to slow down the multiphonon relaxation and as a result have to increase fluorescence quantum yield of the mid IR optical transitions. The directly measured MR rates in the pair M and M' centers gave rather good qualitative agreement between the theory and experiment. Thus, it was experimentally shown that in the series of fluoride crystals with fluorite structure doped with erbium the governing factor influenced the MR rates is the number of phonons  $n$ , which is determined by the cation mass and unit dimension of crystal lattice. An increase of the atom mass of cation and increase of crystal unit dimension  $a$  decreases the maximum phonon frequency  $\omega_{\max}$  and raises the number of phonons  $n$ . This decreases the MR rate and increases the fluorescence quantum yield for  $\text{PbF}_2$  and  $\text{BaF}_2$ . The latter fact is favorable for laser generation in mid IR, especially in the 4–5  $\mu\text{m}$  region, where multiphonon relaxation usually dominates.

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# Green upconverted emission by infrared pump in $\text{Ho}^{3+}$ doped $\text{YAlO}_3$

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Green ( $^5\text{S}_2 \rightarrow ^5\text{I}_8$ ) upconverted emission in  $\text{Ho}^{3+}$  doped  $\text{YAlO}_3$  under infrared pump (in the spectral range of 730–950 nm) is investigated. Polarized excitation and emission spectra together with lifetime and power dependencies were recorded. Possible schemes of upconversion mechanism and numerical simulation based on a rate equation model are presented.

Due to its energy level scheme  $\text{Ho}^{3+}$  could be an interesting ion for hosting upconversion processes. The possibility of upconversion after excitation with wavelengths around 580 nm, 630 nm and 875 nm was reported in [1]. A theoretical study of optical transition probabilities for this system was done in [2].

A series of crystals of Ho-doped (0.1%, 1%, 3% with respect to the Y site)  $\text{YAlO}_3$ , grown by the Czochralski method, were used to investigate the upconverted emission under infrared pump in the spectral range between 730–950 nm. Strong green emission (between 535–560 nm), originating from the  $^5\text{S}_2$ , was achieved after pumping around 750 nm, 840 nm and 910 nm. The green emission after excitation around 840 nm is mainly due to the  $^5\text{I}_6 \rightarrow ^5\text{F}_3$  excited state absorption (ESA), while the excitation around 910 nm brings about a two step absorption process ( $^5\text{I}_8 \rightarrow ^5\text{I}_5$  followed by  $^5\text{I}_6 \rightarrow ^5\text{S}_2$ ). The most intense green emission is achieved for an excitation around 750 nm. Although a very weak ground state absorption band exist in this region, the main role in

excitation is played by ESA1 ( $^5\text{I}_7 \rightarrow ^5\text{S}_2$ ,  $^5\text{F}_4$ ), together with the cross-relaxation processes  $\sigma(^5\text{S}_2, ^5\text{I}_8) \rightarrow (^5\text{I}_7, ^5\text{I}_4)$  (a similar process was reported in  $\text{Ho:YLF}$  [3], generating an avalanche-type mechanism). Additionally, the second excited state absorption ESA2 ( $^5\text{I}_6 \rightarrow ^5\text{G}_6$ ) occurs. For this case the following pumping scheme (Fig 1) is proposed: First, non-resonant ground state absorption (GSA) occurs, by which the  $^5\text{I}_4$  level is excited. A fast phonon relaxation brings the excitation to the  $^5\text{I}_6$  and  $^5\text{I}_7$  levels. From the  $^5\text{I}_7$  level ESA1 and from the  $^5\text{I}_6$  ESA2 take place, populating the  $^5\text{S}_2$  level. The cross-relaxation enhances the population of the  $^5\text{I}_6$  (via nonradiative deexcitation

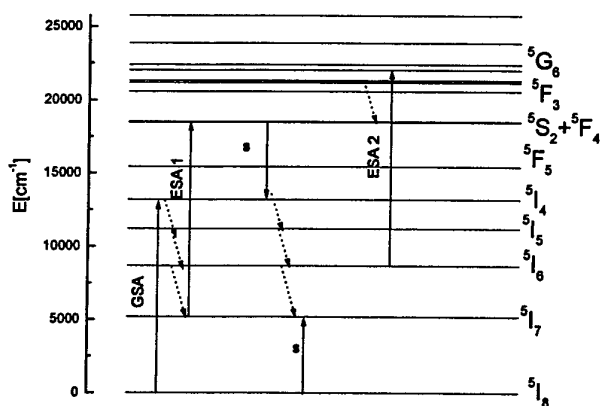


Fig 1. Energy level scheme and upconversion mechanism in  $\text{Ho:YAP}$  under 755nm pump

from  $^5\text{I}_4$ ) and  $^5\text{I}_7$  levels and thus the ESA1 and ESA 2 processes.

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## Optical and spectral properties of unhydrous sol-gel glasses

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The unhydrous silica glass was prepared by hybrid sol-gel process, modified in the part of doping technique. The flowchart of hybrid sol-gel process incorporates the following stages: TEOS hydrolysis in the system  $\text{Si}(\text{OC}_2\text{H}_5)_4 - \text{C}_2\text{H}_5\text{OH} - \text{H}_2\text{O} - \text{HCl}$  with mole ratio 1:2:16:0.01 by vigorous mixing in fluoroplastic reactor in air atmosphere, addition the fumed silica with a specific surface  $200 \text{ cm}^2/\text{g}$  (aerosil T30, Wacker-Chemie GmbH, Germany) into the sol as filler, ultrasonic dispergation with vigorous stirring and centrifugal separation from agglomerates and dust particles/ Then the sol-colloidal system was neutralized up to  $\text{pH}=6.5$  with help of ammonia solution and was cast fluoroplastic moulds to prepare the solid gels shaped as disks and rods. The wet gels were formed during 20–30 min in sealed containers; then the containers were opened and the gels were washed by distilled water.

The resulting gels were dried slowly at  $30\text{--}60^\circ\text{C}$  in the period 7–14 days in air. The drying operation should not cause cracking or warping of large gels.

After drying the xerogels were doped with fluorine by the methods of gas-phase or liquide-phase doping. The fluorinated gels have been densified in air or in helium at the temperature  $1150\text{--}1200^\circ\text{C}$ .

Optical absorption spectra were measured using the glass samples of 2–4 mm thickness with spectrometric devices SPECORD IR-75 in the IR-region and BECKMAN-5270 in the visible and UV-regions.

Hydroxyl content in the dense glass samples was calculated from IR-absorption spectra.

The refractive index (RI) of fluorinated gel-glass was measured by a spatial filtering technique using pure silica glass as a standard, and the RI-profiles in rods, prepared by the method of gas-phase doping, was measured using special equipment (P102 YORK TECHNOLOGY Ltd.).

The effective fluorine and chlorine concentrations in resulting silica gel-glass were measured by the method of micro-X-ray diffraction spectral analysis (MXRSA) (CAMEBAX France).

The process of gas-phase fluorination with using of freon/oxygen mixture results in preparing of silica gel-glass with a level of  $\text{OH}^-$ -groups 1–5 ppm. Liquid-phase doping procedure is probably not able to eliminate the hydroxyls completely and a residual  $\text{OH}^-$ -content consists 30–80 ppm.

The refractive index of the sintered in air silica glass measured  $n_D^{\text{air}}=1.4570$  and was decreased by sintering in helium gas after the fluorination in freon/oxygen atmosphere ( $n_D^{\text{F}}=1.4532$ ). The special technique of duple gas-fluorination was employed for the preparation of silica glass with minimum refraction index value  $n_D^{2\text{F}}=1.4507$  and the hydroxyl level to below 1ppm.

## Progress on erbium 3- $\mu$ m fiber lasers

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In recent years, there has been an increased interest in lasers emitting at 3  $\mu$ m mainly because of their applications in laser surgery. The erbium-doped fluoride fiber is a promising tool for the construction of a compact and efficient all-solid-state laser in this wavelength region. Due to its geometry, the fiber provides large flexibility and potentially high pump- and signal-beam intensities without the drawbacks of thermal and thermo-optical effects that are typically encountered in bulk systems. By a better understanding of the spectroscopy of  $\text{Er}^{3+}$  in ZBLAN, the influence of the fiber geometry on the population mechanisms, and with the recent advances in diode and fiber technology, it has been possible to increase the output power of the erbium 3- $\mu$ m fluoride fiber laser by two orders of magnitude from the 10-mW to the 1-W range. A further increase of the output power by yet another order of magnitude can be expected in the near future.

The possible operational regimes of the erbium 3- $\mu$ m fiber laser are shown in Fig. 1. Depending on dopant concentration, possible codoping by other ions, fiber geometry, resonator configuration, and pump wavelength and intensity, various excitation and relaxation processes can play an important role in this laser. *Left-hand side:* The cascade-lasing regime at low dopant concentration ( $\sim 0.1$  mol.%) in a core-pumped ZBLAN: $\text{Er}^{3+}$  laser. Two loops pumped by ground-state absorption (GSA) and excited-state absorption (ESA) drive the 2.7- $\mu$ m laser transition. The bottleneck of the long  $^4\text{I}_{13/2}$  lifetime is overcome by ESA and the energy upconverted is recycled into the upper laser level by the 1.7- $\mu$ m laser. Experimentally, an output power at 2.7  $\mu$ m of 150 mW and a slope efficiency of 23% were obtained [1]. *Center:* The lifetime-quenching regime at medium dopant concentration ( $\sim 1$  mol.%) in a cladding-pumped ZBLAN: $\text{Er}^{3+}, \text{Pr}^{3+}$  laser. Due to efficient energy transfer (ET) from the  $\text{Er}^{3+}$  lower laser level to the  $\text{Pr}^{3+}$  codopant, the laser operates as a simple four-level laser. Experimentally, an output power at 2.7  $\mu$ m of 1.7 W and a slope efficiency of 17% were obtained [2]. *Right-hand side:* The energy-recycling regime at high dopant concentration ( $\sim 10$  mol.%) in a cladding-pumped ZBLAN: $\text{Er}^{3+}$  laser. Energy-transfer upconversion (ETU) from the lower laser level can recycle energy into the upper laser level and potentially increase the slope efficiency by a factor of two. Predicted slope efficiencies in this regime exceed the Stokes efficiency of the system of 35%. Output powers in the 10-W range can be expected in the near future [3].

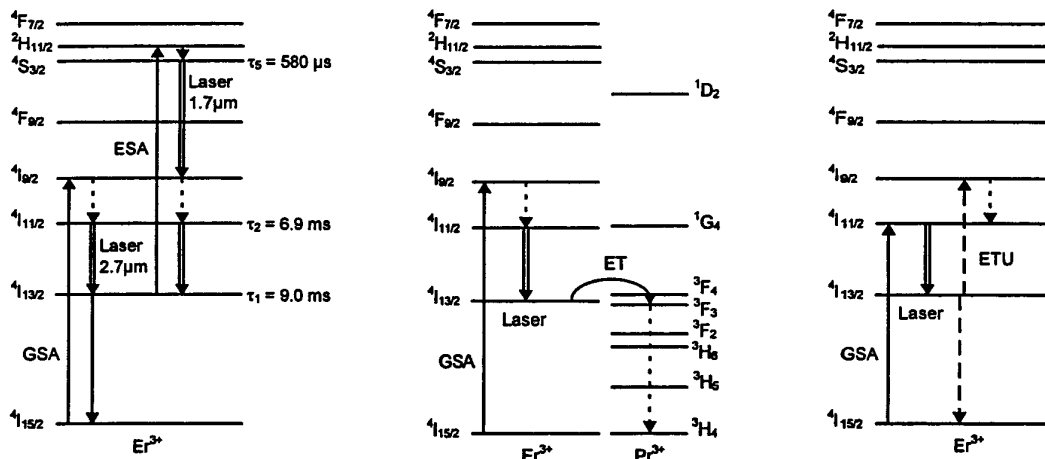


Fig. 1: Operational regimes of erbium 3- $\mu$ m fiber lasers

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## Preparation of RE<sup>3+</sup>-doped silica glasses by colloidal sol-gel process

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The sol-gel technology of glass preparation has received significant attention recently. Sol-gel silica glasses doped with rare-earth (RE<sup>3+</sup>) ions are an important class of optical materials with applications including solid-state lasers, optical waveguides, fiber amplifiers and devices for optical communications.

We used sol-gel technology for the preparation of RE<sup>3+</sup>-doped silica glasses formed from colloidal sols [1].

The fumed silica (SiO<sub>2</sub>), distilled water (H<sub>2</sub>O), surface-active substances and ammonia (NH<sub>4</sub>OH) were used as starting materials for preparation sol. The silica dioxide are dispersed in water with ammonia and surface-active substances. Then HCl or HNO<sub>3</sub> has added in solution for shaping gel.

The xerogels were impregnated with solutions of salts of rare-earth elements (Er<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup> et.al.). The sintering received xerogels was carried out on air or in atmosphere of He at T=1200°C.

In this paper, we describe the preparation of rare-earth-doped silica-gel glasses by colloidal sol-gel process and discuss the spectral-luminescent properties of doped silica glasses.

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## Optical spectroscopy of $\text{Er}^{3+}$ doped $\text{Bi}_{12}\text{SiO}_{20}$ piezoelectric crystal

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The interest in the  $\text{Bi}_{12}\text{SiO}_{20}$  (BSO) piezoelectric crystal doped with  $\text{RE}^{3+}$  ions has increased because of its favorable photo-conductive, photo-refractive, electro-optic and magneto-optic properties for the laser light control. Recently, this crystal has been shown to be a very attractive matrix since stimulated Raman scattering and laser action at room temperature were demonstrated when activated with  $\text{Nd}^{3+}$  ions.

In this work, photoluminescence properties of BSO:Er are investigated under excitation in the near infrared region at low temperature. Up-converted luminescence in the green (~ 555 nm), red (~ 670 nm) and near infrared (~ 860 nm) regions has been observed, as well as a direct infrared emission at about 980 nm. Those emissions have been associated with the  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  (green),  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  (red),  $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$  (~860 nm) and  $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$  (~980 nm) transitions of  $\text{Er}^{3+}$  ions.

Two different types of  $\text{Er}^{3+}$  centers have been detected by site-selective spectroscopy measurements. The mechanisms responsible for the up-conversion processes (excited state absorption and/or energy transfer up conversion) are analyzed and discussed for each type of  $\text{Er}^{3+}$  centers in the crystal.

## Laser gain and site selective spectroscopy of $\text{Nd}^{3+}$ ions in $\text{Gd}_{0.25}\text{Y}_{0.75}\text{Al}_3(\text{BO}_3)_4$

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Yttrium Aluminum Borate (YAB) has been shown to be an excellent non-linear host crystal for  $\text{Nd}^{3+}$  ions in order to produce diode pumped visible laser radiation by several intracavity wave mixing processes inside the laser medium; the so called Self Frequency Doubling (SFD) and Self Frequency Sum Mixing (SFSM) processes<sup>1</sup>.

In this work we have investigated the main laser gain properties of  $\text{Nd}^{3+}$  ions in the  $\text{Gd}_x\text{Y}_{1-x}\text{Al}_3(\text{BO}_3)_4$  (GYAB) non-linear crystal for  $x=0.25$ . In this host, which is isostructural to YAB, it is expected that a 25 % of  $\text{Nd}^{3+}$  ions enter the  $\text{Gd}^{3+}$  lattice site. This lattice ion presents an ionic radius more similar to  $\text{Nd}^{3+}$  than the major  $\text{Y}^{3+}$  lattice ion, then promising an improvement in the gain properties because of these  $\text{Nd}^{3+}(\text{Gd}^{3+})$  ions.

Continuous wave (CW) laser experiments have been carried out by end-pumping with Ti:Sapphire laser (tunable in the diode pumping spectral range) a GYAB:Nd crystal located in a hemispherical cavity. First experiments under non-optimal conditions (neither exact phase matching nor antireflection coatings) show CW laser oscillation at low absorbed power thresholds (18 mW) with an internal loss factor of 5 %  $\text{cm}^{-1}$ . Green laser radiation at 532 nm has been also obtained by SFD.

Site selective spectroscopy experiments are now under way to elucidate on the distribution of the  $\text{Nd}^{3+}$  ions among the available  $\text{Gd}^{3+}$  and  $\text{Y}^{3+}$  lattice sites. We hope to present these results during the meeting time.

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## Influence of preparation redox conditions and composition of Ce-containing silica gel-glass on its absorption spectrum in visible region

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A nature of absorption of Ce-containing glasses in visible region of spectrum is discussed till now. In the present paper, we researched the influence of preparation redox conditions and composition of Ce-containing silica glasses obtained by the direct sol-gel method on the absorption. For the glasses, such absorption is displayed by a broad band with a maximum at  $\lambda \sim 500$  nm. It is established that the preparation of the glasses in strong oxidative conditions (impregnation of monolithic xerogel with a highly-concentrated solution of  $\text{CeO}_2$  in mixture of  $\text{H}_2\text{O}:\text{HNO}_3:\text{HCl}$  and prolonged vitrification of the xerogel in oxygen to a state of transparent glass) leads to the highest peak intensity ( $k \sim 10 \text{ cm}^{-1}$ ) of the broad band. Annealing of the glasses in hydrogen results in attenuation of the band down to its complete disappearance. A co-doping the Ce-containing glasses with Al, La, Nd, Sm, Er, Tm and Yb, is accompanied with attenuation and displacement of the band. Annealing of the glasses in air leads to more complicated 'spectroscopic behavior' of the band. Obtained results refute opinion [1] that the absorption band at  $\lambda \sim 500$  nm for similar glasses is stipulated by formation of the clusters representing the complex groupings of  $\text{Ce}^{4+}\text{-O-Ce}^{3+}$ .

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## Microstructure and luminescence properties of nanocrystalline cerium silicate

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Microstructure and luminescence properties of  $\text{CeO}_2$  nanocrystallites ( $\sim 5$  nm) supported on  $\text{SiO}_2$  and subjected to heat treatment in hydrogen up to  $1100^\circ\text{C}$  were studied by High Resolution Transmission Electron Microscopy (HRTEM) and laser spectrophotometry (lines 266 nm of  $\text{YAG:Nd}^{3+}$  and 308 nm of excimer laser as excitation sources).

It has been found that heating at  $800^\circ\text{C}$  for 4 h resulted in spreading of  $\text{CeO}_2$  over silica and formation of quasi two-dimensional amorphous phase (silicate precursor Fig. left) exhibiting weak, broad emission in violet/blue region 340 – 600 nm. At  $900 - 1050^\circ\text{C}$ , nanocrystalline cerium silicate of undefined structure was formed (Fig. right), that shows strong emission in 340 – 600 nm region. At  $1100^\circ\text{C}$  crystallites of tetragonal A – type  $\text{Ce}_2\text{Si}_2\text{O}_7$  disilicate began to form with only minor changes in PL spectra.

Luminescence properties of the obtained nanocrystalline cerium silicates are compared with those of stoichiometric, bulk compounds: A – type  $\text{Ce}_2\text{Si}_2\text{O}_7$  disilicate and hexagonal  $\text{Ce}_{9.33}(\text{SiO}_4)_6\text{O}_2$  oxyapatite

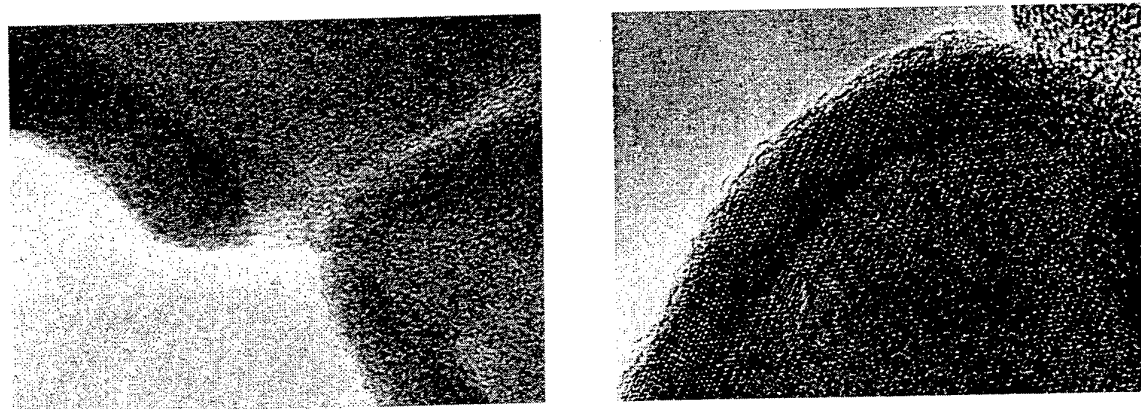


Figure. HRTEM images of nanocrystalline cerium silicates:  $T=800^\circ\text{C}$  (left)  $T=900^\circ\text{C}$  (right).

## Dynamic of the excited states in europium podant, $C_{36}H_{44}Cl_3EuN_8O_5$ , in solid state and solutions

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Heterocyclic ligands are common sensitizers for the lanthanide ions emission under UV irradiation. The lanthanide complexes with these ligands can be used in time-resolved fluoroimmunoassays displaying very high sensitivity. Recently we reported the results of spectroscopic investigation for two types of lanthanide cryptates [1]. Now we present spectroscopic investigation and decay-time results in wide range of temperatures (300, 77, 4 K) for europium podant in solid state, solutions and gel. The compound was synthesized according to procedure described earlier [2]. The luminescence and emission excitation spectra of solid complex and dissolved in  $H_2O$ , MeOH, MeCN have been measured. Two components of  $^5D_0 \rightarrow ^7F_0$  transition have shown an existence of two forms of the complex in aqueous and MeOH solutions but only one in MeCN. The most efficient energy transfer after UV excitation has been shown for the europium complex in aqueous solution but the less for MeCN and solid. The role played by the radiative and nonradiative path in emission intensity has been discussed. The dynamic processes in solutions and gel have been considered and correlated with earlier spectroscopic, NMR and X-ray studies [2, 3, 4]. The pressure and temperature dependence of  $^5D_0 \rightarrow ^7F_0$  transition of Eu(III) complex in water has been measured and thermodynamic parameters ( $\Delta V$ ,  $\Delta H$ ) have been determined.

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## Infrared to visible conversion of radiation in some $\text{Ho}^{3+}$ -doped oxide and fluoride crystals

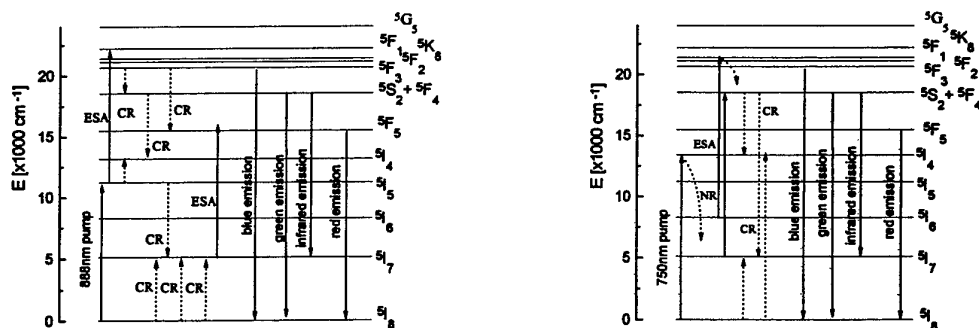
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Due to upconversion processes, photons of the excitation light are converted in the optical material into photons of higher energy. Taking the advantage of the excitation with laser diodes, nowadays commercially available for the near infrared (IR) and IR range, it is expected that upconversion processes can be applied in all-solid-state lasers, detectors for the IR spectral range and other opto-electronic devices.

Within the  $\text{Ho}^{3+}$  ion energy scheme a lot of up-conversion processes can take place resulting in the visible luminescence from the  $^5\text{F}_3$  (blue),  $^5\text{S}_2$  (green), and  $^5\text{F}_5$  (red) energy levels. The efficiency and optimal excitation wavelength for these emissions are strongly dependent on the crystal host, which determines a variety of parameters. These are absorption and excited state absorption cross sections, lifetimes of the emitting and intermediate (storage) energy levels, multiphonon decay rates, and cross relaxation rates determined by resonances in the energy level scheme and by the dopant concentration.

In this presentation upconversion processes taking place in some  $\text{Ho}^{3+}$ -doped fluoride and oxide crystals will be compared for the range of excitation between 740 nm – 980 nm. Depending on the phonon energy, different intermediate energy levels can act as storage levels for excited state absorption processes. For example, in  $\text{Ho}^{3+}:\text{BaY}_2\text{F}_8$  (low phonon energy) the most efficient upconversion is observed due to a two step absorption process:  $^5\text{I}_8 \rightarrow ^5\text{I}_5$  followed by  $^5\text{I}_5 \rightarrow ^5\text{F}_1$ , see Fig.1a. In  $\text{Ho}^{3+}:\text{YLiF}_4$  (medium phonon energy) the strongest visible emission is observed after excitation around 750nm, although at this wavelength only very weak ground state absorption occurs. Here a combination of processes involving multiphonon decay ( $^5\text{I}_4 \rightarrow ^5\text{I}_5 \rightarrow ^5\text{I}_6 \rightarrow ^5\text{I}_7$ ), cross relaxation ( $(^5\text{S}_2, ^5\text{I}_8) \rightarrow (^5\text{I}_4, ^5\text{I}_7)$ ) and excited state absorption ( $^5\text{I}_7 \rightarrow ^5\text{S}_2$ ) takes place, see Fig.1b. In  $\text{Ho}^{3+}:\text{LiTaO}_3$  (high phonon energy), the upconverted visible emission practically does not occur after excitation into the  $^5\text{I}_5$  multiplet. The strongest green emission is observed after excitation into the  $^5\text{I}_4$  multiplet. In  $\text{Ho}^{3+}:\text{YVO}_4$  (high phonon energy) there is practically no green emission after excitation in the whole IR excitation range under investigation.



a)

b)

Fig.1. Schematic diagram of energy levels and processes involved in  $\text{Ho}^{3+}:\text{BaY}_2\text{F}_8$  (a),  $\text{Ho}^{3+}:\text{YLiF}_4$  (b); ESA - excited state absorption, CR - cross-relaxation processes.

## Crown ether complexes with divalent europium

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In this communication the crystal structures and the luminescent properties of three complexes of Eu(II) with crown ethers will be presented. The investigated compounds are:

1. A complex of Eu(II) with benzo-18-crown-6, with the metal-to ligand ratio 1:1. The metal ion coordination environment comprises 3 water molecules;
2. A complex with the same ligand, with metal-to ligand ratio 1:2, with a similar metal surrounding;
3. An anhydrous 1:2 Eu – benzo-15-crown-5 complex. The metal ion is surrounded by 10 ether oxygen atoms only.
4. All three compound display blue-violet luminescence near 420-430 nm of the Eu(II) f-d transition.

## **Ternary orthophosphates of the $\text{Ba}_3\text{Y}_{1-x}\text{Nd}_x(\text{PO}_4)_3$ family as possible powder laser materials**

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Ternary orthophosphates  $\text{Ba}_3\text{Y}(\text{PO}_4)_3$  doped with 0.05, 0.1, 0.15 and 0.2  $\text{Nd}^{3+}$  weight content were synthesized. The powder samples were separated according to their grain size and compared using spectroscopic data. Their IR, Raman, electron absorption and luminescence spectra were measured at room and liquid helium temperature. The excited states of the  $\text{Nd}^{3+}$  ions were characterized by means of decays curves of the life times. The possibility of the application of these materials as powder laser is discussed.

## An EPR study of several gadolinium(III) dicarboxylates

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The EPR studies of various gadolinium complexes have been the aim of our previous papers [1-2]. In this paper complexes of Gd(III) with four dicarboxylic acids (IDA – iminodicarboxylic, DPA – dipicolinic, DGA – diglycolic, and TDA – thiodiglycolic) having N, O and S donor atoms, potentially liganding the Gd(III) ion have been used for EPR studies.

Our previous investigations, based on luminescence spectroscopy of the Eu(III) ion and FTIR spectra, have shown that the donor atoms of N and O are bound to the lanthanide ions, in tridentate (iminodicarboxylic, diglycolic and dipicolinic acid) ligands, whereas S is not bound to these ions, thus thiodiglycolic acid coordinates as a bidentate ligand [3].

The EPR measurements were performed on spectrometers working on X (9.4 GHz) and Q (35 GHz) – bands. The spectra on X band, recorded for Gd-IDA, Gd-DPA and Gd-DGA complexes consist of several lines with values of g-factor characteristic for complexes having none water molecules in the inner coordination sphere of the Gd(III) ion. In the case of Gd-TDA complex a very poor resolved spectrum having only two broad lines, with  $g = 4.89$  and  $2.0$ , was obtained.

Analysing zero-field splitting (ZFS) parameter,  $D$ , for the compounds studied, the following  $D$  values have been estimated for: DGA – 1200 MHz, Gd-IDA – 1150 MHz, DPA – 1350 MHz, TDA – 950 MHz, respectively. The  $D$  values indicate that in presence of S donor atom in the complex the smallest deformation from the cubic symmetry of the system, what can support the earlier observation that S atom doesn't bound the Ln(III) ions [3].

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## Cross-relaxation effects on spectra of the excitation and luminescence kinetics of an $\text{Tm}^{3+}$ ion in gadolinium oxychloride

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The photoluminescence spectra as well as the excitation spectra and the kinetics of photoluminescence for different bands of the emission spectrum of the  $\text{Tm}^{3+}$  ions have been measured depending on their concentration in gadolinium oxychloride.

The analysis of the concentration effects in the excitation spectra of the IR luminescence of  $\text{Tm}^{3+}$  ions for monitoring in the 1,8  $\mu\text{m}$  region shows that with increasing concentration a redistribution of the bands intensity for benefit of the UV area indicating to the enhancement of the role of the multistage cross-relaxation in the populating of the lower excited luminescent levels and in the increases in the IR luminescence quantum yield. The concentration curves describing the changes in the UV bands intensity of the excitation spectrum or IR bands intensity in the luminescence spectrum, have a maximum in the interval 5 – 10 mol. %  $\text{Tm}^{3+}$ . The sharpest increase in the IR luminescence intensity is observed at excitation in UV bands of the absorption spectrum that corresponds to the mechanism of three-stage cross-relaxation populating of the lowest luminescent level. In the excitation spectrum of the IR luminescence line at  $\lambda = 1,19 \mu\text{m}$  only the band in the blue area of the absorption spectrum of the  $\text{Tm}^{3+}$  ion, manifests itself with increasing concentration corresponding to the most resonant cross-relaxation channel of the luminescent  $^3\text{H}_5$  level population. In the luminescence spectrum the line at  $\lambda = 1,19 \mu\text{m}$  is observed only at excitation in a blue band of the absorption spectrum ( $^1\text{G}_4$  level of the  $\text{Tm}^{3+}$  ion).

With the use laser excitation the luminescence rise and decay kinetics in the visible and IR areas of spectrum has been investigated. The comparison of the kinetic curves for various bands of the luminescence spectrum in the visible and IR areas also shows, that the decay of the high excited levels occurs by the cross-relaxation followed by the populating of lower levels of  $\text{Tm}^{3+}$  ion. The time of the visible luminescence decay (for example, at 460 nm) at excitation in the UV of absorption band (354 nm) decrease from 7,1 to 1  $\mu\text{s}$  on the increase in tulium concentration from 0,01 to 50 mol. %. The time of the luminescence rise (reaching the maximum value of intensity) also is decreased from 0,8 to 0,1  $\mu\text{s}$ . The time of IR luminescence decay ( $\lambda = 1,8 \mu\text{m}$ ) (its initial exponential stage) is decreased from 4,2 to 0,75  $\mu\text{s}$  in the interval of the tulium concentration from 1 to 10 mol.%  $\text{Tm}^{3+}$ , while the rise time is decreased from 190 to 95  $\mu\text{s}$ . The luminescence rise and decay curves are not described by one-exponential function.

Thus, for the samples of gadolinium oxychloride activated by the  $\text{tm}^{3+}$  ions, by the sharp enhancement of the luminescence in the 1,8  $\mu\text{m}$  region is observed in the interval of concentration 0,1 – 5 mol. % at excitation in uv bands of the absorption spectrum, caused by the cross-relaxation mechanism of the luminescent level populating, resulting in the multiplication of the low energy electronic excitations.



## Spectra and details of the structure of europium aliphatic carboxylates with 1,10-phenanthroline derivatives

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The goal of this work – to investigate the effect of donor-acceptor and steric properties of inequivalent ligands on the structure of europium aliphatic carboxylates with 1,10-phenanthroline and its derivatives. X-ray and spectroscopic information on the peculiarities of the structures of compounds was obtained and used to analyse the reciprocal influence of inequivalent ligands.

The luminescence, excitation of luminescence, IR and Raman spectra of variety of compounds  $\text{Eu}(\text{RCOO})_3\text{Ph}$ , (R –  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_2\text{H}_4\text{OH}$ ,  $-\text{C}_5\text{H}_{11}$  for acetate, propionate, lactate and capronate compounds, Ph – six phenanthroline derivatives) were examined.

A crystal structure of the europium acetate  $\text{Eu}(\text{CH}_3\text{COO})_3\text{Phen}$  was solved by X-ray method. The compound consists of dimers in analogy to the capronate  $\text{Eu}(\text{C}_5\text{H}_{11}\text{COO})_3\text{Phen}$ . There are three types of coordination of the carboxyl groups.

Dependence of the Stark splitting of the  $\text{Eu}^{3+}$  electronic levels on variation of the ligands was examined. Crystal field parameters for model complexes were calculated. The position of the UV wide band of phenanthroline derivatives in the excitation spectra was investigated. The vibration bands of both ligands in IR and Raman spectra indicating on details of the structure of compounds were analysed.

Inequivalence of the carboxylic groups and the relative strength of bonds of the metal ion with two kinds of ligands were estimated in function of size, polarizability, donor-acceptor properties of the ligands. The effect of carboxyl radical on the nearest surroundings of  $\text{Eu}^{3+}$  ion in  $\text{Eu}(\text{RCOO})_3\text{Ph}$  is more profound than the effect of phenanthroline substituents. Steric factors are as significant as the donor-acceptor properties of the phenanthroline derivatives in creation of the structure of  $\text{Eu}(\text{CH}_3\text{COO})_3\text{Ph}$  compounds. The acetates with electrophilic  $\text{NO}_2$ -groups and with bulky substituents in the phenanthroline molecules can be characterised by the highest inequivalence of Eu-O bonds. Strongly polarised carboxyl groups are present in these compounds.

Influence of the long aliphatic radical on the structure of europium capronate consists in equalisation of the oxygen effective charges of the tridentate carboxyl groups and in weakening the metal polarising effect on the phenanthroline molecules. Due to higher mobility of the capronate anions a partial disorder of atoms, situated at the outer coordination sphere, is displayed both in the spectra, and in the X-ray data. The arrangement of the effective charges of the first coordination sphere of the metal ion is the most symmetric in europium propionate.

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## Isotopic effect in the vibronic spectra of lanthanide compounds

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The effect of the kinematic of the crystal lattice on vibronic spectra of europium ( $\text{Eu}^{3+}$ ) and  $\text{Eu}^{3+}$  doped lanthanide ( $\text{Ln}^{3+}$ ) compounds was examined experimentally. Changes in the vibronic excitation spectra of  $\text{Eu}^{3+}$  were studied in two cases: influence of purely kinematic factor (isotopic substitution) and the kinematic changes at the slight changes of potential forces (quasi-isotopic substitution in isostructural compounds).

It was demonstrated, that isotopic substitution of the ions of the crystal lattice gives rise not only to a change of the vibration frequencies in vibronic sidebands, but also causes a change of the value of electron-phonon interaction, that displays in changing the integral intensity of the vibronic sidebands and sometimes in changing the intensity of the individual vibronic satellites.

Vibronic spectra of more than 15 pairs of natural and isotopic substituted europium compounds, related to the different kinds of crystal structures: mononuclear, binuclear, netlike ones, were studied. The vibronic sidebands of the  ${}^7\text{F}_0 - {}^5\text{D}_0$ ,  ${}^5\text{D}_1$ ,  ${}^5\text{D}_2$  transitions of  $\text{Eu}^{3+}$  ions were investigated. IR spectra were analysed to facilitate the assignments of vibronic satellites. Europium nitrates, formates, acetates, acid oxalate, ethyl sulphate, bromate,  $\beta$ -diketonates and other compounds were investigated. In most cases the substitution of deuterium for hydrogen were applied to get a large difference in the vibration amplitudes. This substitution was used in such ligands as molecules of water, 2,2'-bipyridine, anions of carboxylic acids. A factor of decreasing the relative intensity of the vibronic sidebands lies between the limits  $\sim 1,2$  and  $\sim 7$  for different compounds under investigation. The largest change of the intensity of vibronic sidebands was observed in pairs of formates  $\text{Eu}(\text{HCOO})_3$  and  $\text{Eu}(\text{DCOO})_3$ , having the tridentate-bridging coordination of the formate anions and a netlike structure.

Manifestation of the isotopic substitution in the vibronic spectra is determined by the character of the crystal lattice dynamics. Decrease of the electron-phonon interaction with the increase of the isotope weight is caused by the decrease of the contribution of the crystal lattice vibrations in the displacements of atoms of the complex formed by the  $\text{Ln}^{3+}$  ion and its neighbouring atoms. The value of the effect depends on different structural factors: the kind of crystal lattice, the manner of ligand coordinations, the number of coordination sites in surroundings of lanthanide ions, occupied by the ligand, etc.

The work was supported by the Russian Foundation for Basic Research (grants N 00-02-16655 and N 01-02-16837).

## Site symmetries of $\text{Cu}^{2+}$ ions in $\text{LiNbO}_3$ crystals

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Doped with  $\text{Cu}^{2+}$  ions ionic crystals have their absorption bands, which are due to inner d-d transitions, at near-infrared region. In  $\text{LiNbO}_3$  congruent crystal, such d-d absorption bands are observed at about 1000 and 2000 nm. The two bands are well separated from each other.

At low temperatures the 1000 nm band is about ten-times bigger than the 2000 nm one. It has been observed that the 2000 nm band has a single non-structural Gaussian shape. Petrosyan et al. (Petrosjan A.K, Hachatrian and R.M Sharojan, *Phys. Stat. Sol. b* **122** (1984) 725) observed a triplet structure for the 1000 nm band. Kobayashi et al. (T. Kobayashi, K. Mutto, J. Kai and A. Kawamori, *J. Mag. Res.* **34** (1970) 459) also observed triplet structure, but its line shape is not the same as the line shape observed by Petrosyan et al.

We observed another type of triplet structure in some crystals, and a doublet structure in the other crystals. The observed line shape of the 1000 nm band depends on the condition of crystal growth and concentration of  $\text{Cu}^{2+}$  ions. It is suggested that different crystal growth conditions give rise to different  $\text{Cu}^{2+}$  location in  $\text{LiNbO}_3$  lattice sites.

# Opposite parity $4f^{n-1}5d^1$ states of $Ce^{3+}$ and $Pr^{3+}$ in $MSO_4$ (M: Ca, Sr, Ba)

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Measurements on the opposite parity  $4f^{n-1}5d^1$  state of  $Ce^{3+}$  and the  $4f^15d^1$  state of  $Pr^{3+}$  in three different sulphate hosts are presented. The energy position in excitation comparing  $Ce^{3+}$  and  $Pr^{3+}$  in the same host is different, but the overall spectrum and crystal-field splitting show strong similarities.

The energy difference of the first  $4f^{n-1}5d^1$  band in  $Pr^{3+}$  and  $Ce^{3+}$  was found to be a constant value. This energy difference for  $CaSO_4$  is about  $12\,500\text{ cm}^{-1}$ , which is in good agreement with the value of  $12\,240 \pm 750\text{ cm}^{-1}$  for  $\Delta E_{Ce,Pr}$  as is found by Dorenbos in various hosts<sup>1</sup>. The excitation spectra of  $CaSO_4$  doped with  $Pr^{3+}$  and  $Ce^{3+}$  measured at  $T=10\text{ K}$  are shown in Fig. 1.

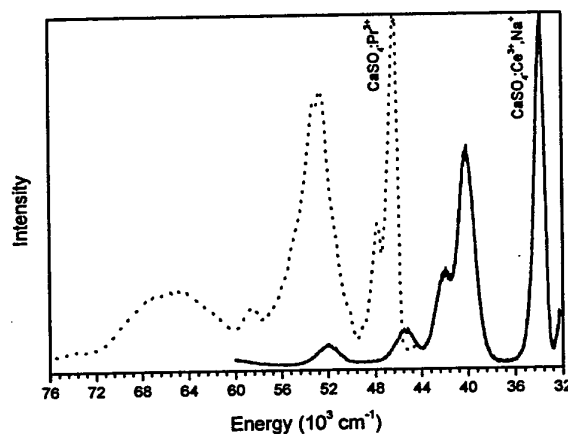


Figure 1:  $4f^{n-1}5d^1$  excitation spectrum of  $CaSO_4:Ce^{3+}, Na^+$  ( $n=1$ ,  $\lambda_{em}=326.5\text{ nm}$ ) and  $CaSO_4:Pr^{3+}$  ( $n=2$ ,  $\lambda_{em}=230\text{ nm}$ )

Prediction of the energy position of the  $Pr^{3+}$  opposite parity state from  $Ce^{3+}$  can be useful help in the search for new quantum cutting materials using  $Pr^{3+}$ . The position of the  $4f^15d^1$  state will determine if the material, when doped with  $Pr^{3+}$ , may show quantum cutting behaviour. When the  $4f^15d^1$  state of  $Pr^{3+}$  is at lower energy than the  $4f^2\ ^1S_0$  state, quantum cutting is not possible. Excitation in the  $4f^15d^1$  state of  $Pr^{3+}$  results in parity allowed  $4f^15d^1 \rightarrow 4f^2$  emission mostly situated in the vacuum ultraviolet (VUV) spectral region. This is the case for  $CaSO_4$ , where the  $5d^1$  crystal field splitting is large (co-ordination number: 8). The  $4f^15d^1$  state for  $Pr^{3+}$  in  $SrSO_4$  and  $BaSO_4$  (co-ordination number: 12) is at high energy. When exciting in this state, two-step emission from  $^1S_0 \rightarrow ^1I_6$  and  $^3P_0, ^1D_2 \rightarrow ^3H_4$  can occur as was first reported in 1974 by both Piper and Sommerdijk for  $YF_3:Pr^{3+}$ <sup>2,3</sup>. The emission properties of  $CaSO_4$ ,  $SrSO_4$  and  $BaSO_4$  doped with  $Pr^{3+}$  are reported and will be related to the position of the opposite parity state.

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## Temperature dependencies of excited states lifetimes and relaxation rates of 3–5 phonon (4–6 $\mu\text{m}$ ) transitions in the YAG, LuAG, YLF crystals doped with trivalent holmium, thulium and erbium

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The temperature dependencies of the nanosecond multiphonon relaxation (MR) rates of the  $^3\text{F}_3$  state of  $\text{Tm}^{3+}$  in the YLF crystal and of the  $^5\text{F}_5$  state of  $\text{Ho}^{3+}$  ion in the YAG and LuAG crystals and of the microsecond MR rates of the  $^4\text{F}_{9/2}$  ( $^2\text{H}_{9/2}$ ) state of  $\text{Er}^{3+}$  ions in YLF were measured in the wide temperature range using direct laser excitation and selective fluorescence kinetics decay registration. For YLF the observed relations are explained by 4-phonon process in the frame of a single frequency model with  $h\omega_{\text{eff}} = 450 \pm 30 \text{ cm}^{-1}$  for the  $^3\text{F}_3$  state of  $\text{Tm}^{3+}$  and by 5-phonon process with  $h\omega_{\text{eff}} = 445 \text{ cm}^{-1}$  for the  $^4\text{F}_{9/2}$  ( $^2\text{H}_{9/2}$ ) state of  $\text{Er}^{3+}$ . For YAG and LuAG crystals these dependencies are explained by the 3-phonon process with  $h\omega_{\text{eff}} = 630 \text{ cm}^{-1}$ . The decrease of the relaxation rate with the temperature in the range from 13 to 80 K was observed for the  $^4\text{F}_{9/2}$  ( $^2\text{H}_{9/2}$ ) state of  $\text{Er}^{3+}$  in the YLF crystal. It is explained by the redistribution of excited electronic states population of erbium ions over the higher lying Stark levels with different multiphonon relaxation probabilities. A good fit of experimental temperature dependence (including the dropping part of the experimental curve) was obtained for single frequency model ( $h\omega_{\text{eff}} = 450 \text{ cm}^{-1}$ ) with  $W_{01} = 7.6 \cdot 10^4 \text{ s}^{-1}$  and  $W_{02} = 6.7 \cdot 10^4 \text{ s}^{-1}$  accounting Boltzman distribution of population over two excited Stark levels of the excited state of erbium ions. Accounting of the third Stark level improves the fit. For the latter case it was found that the probability of spontaneous multiphonon emission from different Stark levels might differ within one order of magnitude ( $W_{01} = 7.7 \cdot 10^4 \text{ s}^{-1}$ ,  $W_{02} = 4.8 \cdot 10^4 \text{ s}^{-1}$  and  $W_{03} = 10.0 \cdot 10^4 \text{ s}^{-1}$ ). Employment of this model improves the fit between the experiment and the theory for the  $^5\text{F}_5$  state of  $\text{Ho}^{3+}$  ion in YAG as well. Strong influence of the parameters of the nonlinear theory of multiphonon relaxation, i.e. the reduced matrix elements  $U^{(k)}$  of electronic transitions and the phonon factor of crystal matrix  $\eta$  on the spontaneous MR rates was observed experimentally. The smaller these parameters the slower the spontaneous multiphonon relaxation  $W_0$ . This fact can be used for searching new active crystal laser media for the mid IR generation.

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## Luminescence of $\text{BiB}_3\text{O}_6:\text{Eu}^{3+}$

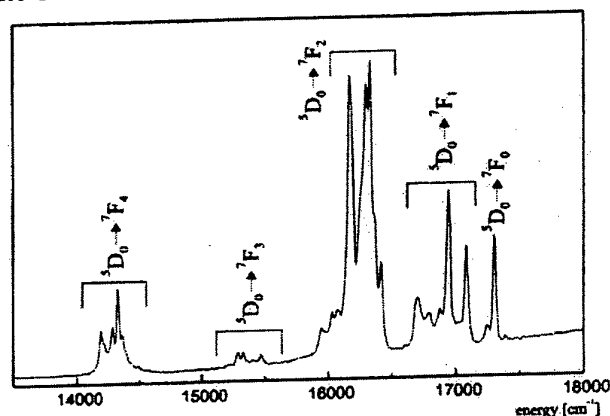
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Due to its excellent linear and nonlinear optical properties  $\text{BiB}_3\text{O}_6$  (BIBO) is a new, very promising material for nonlinear optical applications [1, 2]. Crystal of BIBO were doped with various trivalent rare earth ions and their spectroscopic properties were investigated recently [3]. Research concerning their luminescence properties of  $\text{BiB}_3\text{O}_6:\text{RE}^{3+}$  is motivated by the question about its potential for the development of a new laser which works in the visible range and can be pumped by diode lasers. The visible radiation results from the self frequency doubling of the infrared laser emission.

Large single crystals of  $\text{BiB}_3\text{O}_6:\text{Eu}^{3+}$  were grown by the top-seeded growth technique to dimensions up to  $8 \times 10 \times 15 \text{ mm}^3$ . Luminescence measurements were carried out using a SPEX DM3000F fluorometer equipped with two 0.22m double monochromators at 4K. The excitation as well as emission spectra show that  $\text{Eu}^{3+}$  occupies two different crystallographic sites in the host lattice. The point symmetry of the sites can be determined from the emission spectra by exciting only ions of one site. With respect to the number of  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  lines due to transitions to different crystal field levels there is one site with symmetry  $\text{C}^2$  which is likely the  $\text{Bi}^{3+}$  site. The other site occupied by  $\text{Eu}^{3+}$  turned out to be of higher point symmetry, probably  $\text{C}_3$  or  $\text{C}_{3v}$ . On account of the monoclinic symmetry of  $\text{BiB}_3\text{O}_6$ , this is not a regular site of the host lattice.



Emissionspectrum of  $\text{BiB}_3\text{O}_6:\text{Eu}^{3+}$ , both sites excited, 4K

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## Excited state absorption in materials containing the $\text{Cr}^{3+}$ and $\text{Cr}^{4+}$ ions

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The ground state absorption (GSA), the excited state absorption (ESA) and fluorescence properties (emission spectra and decays) of  $\text{Cr}^{3+}$ ,  $\text{Cr}^{4+}$ -doped single crystals:  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG),  $\text{Y}_3\text{Ga}_5\text{O}_{12}$  (YGG) and  $\text{SrGaGd}_3\text{O}_7$  (SGG) have been studied at various temperatures in broad spectral range (300-1700 nm). In all the measured characteristics of those crystals we have observed features, which could be ascribed to both  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$ . In this work, we put a special stress upon the ESA measurements. The measurements were performed by continuous wave pump-and-probe phase sensitive technique using an Ar-laser (excitation directly into the ion) and tungstate lamp, or by pulsed technique using an excimer laser (UV excitation) and Xe-flash lamp. Relations between spectral responses of the  $\text{Cr}^{3+}$  and  $\text{Cr}^{4+}$  ions in different matrices under various excitations are observed and commented.

## Infra-red to visible up-conversion in holmium doped materials

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In the up-conversion processes excitation light is converted into light having wavelength shorter than the excitation wavelength. In a rare earth doped crystal the up-conversion process was first described in 1959 [1] in a paper on quantum counters. These processes are very interesting because they are essential for operation of several classes of optical devices such as: temperature sensors, IR quantum counter detectors, three different colour emitting phosphors, compact visible or UV solid state lasers and others, thus rare earth doped materials are intensively investigated. Trivalent holmium ion has several energy levels [2] in the energy range from the near IR to near UV spectral region so many emission and absorption transitions are possible and several mechanisms of up-conversion exist. In this work we report on our investigations of  $\text{Ho}^{3+}$  doped oxide crystals – YAP (Yttrium Aluminium Perovskite –  $\text{YAlO}_3$ ), YAG (Yttrium Aluminium Garnet –  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ),  $\text{SrLaGa}_3\text{O}_7$  and  $\text{SrLaGaO}_4$ , and fluoride materials – YLF (Yttrium Lithium Fluoride –  $\text{LiYF}_4$ ) and ZBLAN ( $\text{ZrF}_4 + \text{BaF}_2 + \text{LaF}_3 + \text{AlF}_3 + \text{NaF}$  glass) – under excitation in the 745–788 nm, 862–998 nm and 960–990 nm spectral ranges. The possible mechanisms of up-conversion are discussed. Changing of the holmium luminescence colour between yellow and green was observed after 862 – 988 nm excitation, investigated and explained. For discussing the up-conversion pathways we used; the Judd-Ofelt [3,4] approximation to determine the excited state absorption cross section and Auzel [5,6] approximation to calculate the cross section of nonresonant side-band absorption.

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## Spectroscopic studies of $\text{Er}^{3+}$ centers in $\text{KYF}_4$

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Fluoride compound  $\text{KYF}_4$  is very attractive for developing upconversion-pumped solid-state and VUV lasers. The structure study shows that  $\text{KYF}_4$  is a multisite crystal and  $\text{Y}^{3+}$  ions occupy six crystallographic sites with two types in the crystal [1]. However, when rare earth ions were introduced into the crystal, they were not distributed among all the six sites equally. Bouffard and co-workers studied site-selective upconversion excitation of  $\text{KYF}_4:\text{Er}^{3+}$  and found that the emission spectrum can only be interpreted by considering that it is due to two sites [2].

We present here the detailed spectroscopic study of  $\text{Er}^{3+}$  centers in  $\text{KYF}_4$ . The sample was grown by the hydrothermal synthesis technique with concentration of 5%. To benefit from the narrowness of the inhomogeneous energy transitions and to reduce phonon effect, all the experiments were conducted at 12K. Through absorption, excitation and emission spectra at 12K, we got the conclusion that in the crystal  $\text{KYF}_4:\text{Er}^{3+}$  (5%),  $\text{Er}^{3+}$  ions occupy two sites. By using site selective excitation (emission) at 12K, emission (excitation) spectra origin in two different crystallographic sites were separated clearly (Fig.1). The lifetime of the  $^4\text{S}_{3/2}$  levels of the two sites are 0.53 and 0.82ms. The mechanism of green upconversion luminescence under red excitation is explained by  $^4\text{F}_{9/2}, ^4\text{F}_{9/2} \rightarrow ^4\text{F}_{7/2}, ^4\text{I}_{11/2}$  cross-relaxation process.

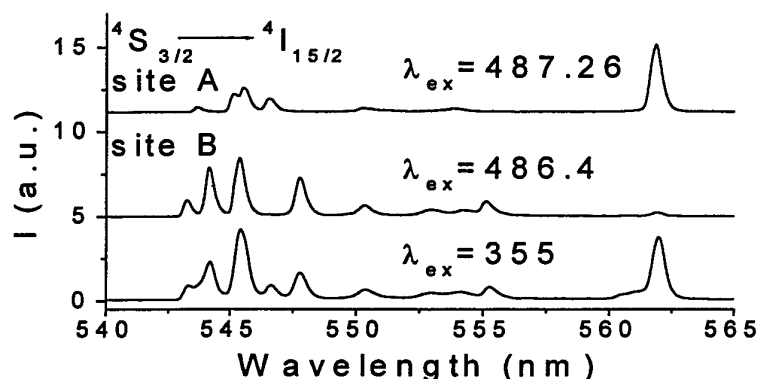


Fig.1 Emission spectra of  $\text{KYF}_4:\text{Er}^{3+}$  (5%) at 12K under selective excitation to site A, site B and under 355nm excitation.

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## Excited state absorption and passive Q-switch performance of $\text{Co}^{2+}$ doped oxide crystals

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In this report we have studied excited state absorption, bleaching relaxation, and passive Q-switch operation of the tetrahedral  $\text{Co}^{2+}$  ion in different oxide crystals  $\text{LiGa}_5\text{O}_8$  (LGO),  $\text{MgAl}_2\text{O}_4$  (MALO), and  $\text{LaMgAl}_{11}\text{O}_{19}$  (LMA) under excitation in the  $^4\text{A}_2 \rightarrow ^4\text{T}_1(^4\text{F})$  transition in the near infrared.

The excited state absorption band observed at 740 nm for the  $\text{Co}^{2+}$ :LGO, 730 nm for the  $\text{Co}^{2+}$ :MALO, and at 710 nm for the  $\text{Co}^{2+}$ :LMA was assigned to the  $^4\text{T}_2 \rightarrow ^4\text{T}_1(^4\text{P})$  transition of the  $\text{Co}^{2+}$  ion. The upper limit of the lifetime of the  $^4\text{T}_1(^4\text{F})$  state was estimated to be ~20 ps. The lifetime of the  $^4\text{T}_2$  level was measured to be  $350 \pm 40$  ns for the  $\text{Co}^{2+}$ :MALO,  $130 \pm 20$  ns for the  $\text{Co}^{2+}$ :LGO, and  $200 \pm 20$  ns for the  $\text{Co}^{2+}$ :LMA using pump-probe technique.

From the absorption saturation measurements the ground state  $\sigma_{\text{gsa}}$  and excited state absorption  $\sigma_{\text{esa}}$  cross sections of the  $\text{Co}^{2+}$ :LGO,  $\text{Co}^{2+}$ :MALO and  $\text{Co}^{2+}$ :LMA crystals at the wavelengths 1.34  $\mu\text{m}$  and 1.54  $\mu\text{m}$  were estimated to be  $\sigma_{\text{gsa}} = (1.2-3.5) \times 10^{-19} \text{ cm}^2$  and  $\sigma_{\text{esa}} = (1-5) \times 10^{-20} \text{ cm}^2$  depending on crystal host and wavelength.

With the  $\text{Co}^{2+}$ :LGO,  $\text{Co}^{2+}$ :MALO and  $\text{Co}^{2+}$ :LMA crystals as saturable absorbers passive Q-switching of a 1.34- $\mu\text{m}$   $\text{Nd}^{3+}$ : $\text{YAlO}_3$  and 1.54- $\mu\text{m}$   $\text{Er}^{3+}$ :glass flash-lamp pumped lasers was demonstrated. Q-switched laser pulses of 60 ns in duration and up to 20 mJ energy at 1.34  $\mu\text{m}$  and 60 ns in duration and up to 8 mJ in energy at 1.54  $\mu\text{m}$  were obtained.  $\text{Co}^{2+}$ :MALO crystal was also used to Q-switch a diode pumped 1.35- $\mu\text{m}$   $\text{Nd}:\text{KGd}(\text{WO}_4)_2$  laser. The intracavity radiation focusing on the Q-switch was not required. Q-switched pulses with duration of 250 ns were obtained at the repetition rate up to 100 kHz with maximum Q-switching conversion efficiency of 16%.

## Radiation and temperature induced recharging of manganese ions in Mn-doped $\text{YAlO}_3$

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The high diffraction efficiency in visible and infrared regions and high stability of the recorded grating at room temperature demonstrated in Mn-doped  $\text{YAlO}_3$  (YAP) [1] have showed a potential of this material for holographic recording and optical storage. The grating observed in YAP-Mn is associated with the refractive index grating and in a lesser degree with the absorption grating.

The changes of optical absorption of YAP-Mn under  $\text{Ar}^+$ -laser illumination ( $\lambda=514$  nm that corresponds to writing beam) and spectroscopy of manganese ions in YAP in different valent states ( $5+$ ;  $4+$ ;  $3+$ ;  $2+$ ) were studied earlier [1,2].

Mn-single doped YAP crystals and YAP-Mn crystals co-doped with Ce and Ca studied in the present work were grown by the Czochralski technique in nitrogen atmosphere with up to 0.5 % of oxygen [1].

In the present work the results of influence of  $\gamma$ -irradiation and high-temperature redox treatments on optical absorption of Mn-doped YAP are presented as well as results on thermally stimulated destruction of the induced absorption and thermoluminescence of the crystals.

Under  $\gamma$ -irradiation of YAP-Mn the same recharging processes of Mn ions (concerned with ionization of  $\text{Mn}^{4+}$ ) take place as in the case of  $\text{Ar}^+$ -laser illumination ( $\lambda=514$  nm). The influence of point defects (color centers (CC)) peculiar to YAP structure on the stable absorption of YAP-Mn induced by radiation or high-temperature treatments is imperceptible, whereas in YAP-Mn, Ca, Ce along with the recharging of Mn the participation of CC (particularly F-type centers that absorb in visible) is observed. None stable changes of absorption in visible region due to recharging of Mn ions or CC peculiar to YAP were observed in YAP-Mn, Ce.

The optical absorption induced in the  $20000\text{--}12000\text{ cm}^{-1}$  region in YAP-Mn destroys in two stages with maximum speed at  $\sim 410$  K and  $\sim 520$  K. At that the destruction of bands with maximums at  $18800\text{ cm}^{-1}$  and  $15500\text{ cm}^{-1}$  (that correspond to intra-center absorption of  $\text{Mn}^{3+}$  and  $\text{Mn}^{5+}$  respectively [2]) takes place simultaneously at least in the first stage.

The same two peaks at  $\sim 410$  K and  $\sim 520$  K are observed in thermal glow curves of YAP-Mn. At the first stage the crystal gives only red light that corresponds to intra-center luminescence of  $\text{Mn}^{4+}$ , and at the second stage the crystal gives both red light and yellow light that corresponds to  $\text{Mn}^{2+}$  luminescence. The obtained results testify that  $\text{Mn}^{2+}$  ions participate in the recharging processes only in the second stage of warming. On the basis of the experimental results the possible mechanisms of recharging of manganese ions are discussed.

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## Charge transfer band in spectrum of sodium-europium salt of cinchomeronic acid

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The absorption, luminescence, luminescence excitation, and IR spectra of the lanthanide (europium, terbium etc) salts of pyridine-dicarboxylic (dipicolinic, quinolinic, and cinchomeronic) acids were investigated. Splittings and shifts of the vibration bands of ligands in IR spectra of the salts witness about inequivalence and coordination of carboxylic groups in salts under investigation. The Stark components of the bands in spectra of  $\text{Eu}^{3+}$  in dipicolinic salts of formula  $\text{M}_3\text{Eu}(\text{dipic})_3 \cdot 12\text{H}_2\text{O}$ ,  $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$  were analysed. The Stark components of the  $\text{Eu}^{3+}$  transitions in spectra of cinchomeronic salts are broadened due to partial disorder in the intermolecular hydrogen bonds.

A band of the charge transfer from the ligand to europium ion was observed in the 360–400 nm region of the excitation and absorption spectra of hydrate of sodium-europium salt of cinchomeronic (pyridine-3,4-dicarboxylic) acid. That band was absent in the spectra of corresponding sodium-europium dipicolinic (pyridine-2,6-dicarboxylic) and quinolinic (pyridine-2,3-dicarboxylic) salts and in spectra of all three sodium-terbium salts of the pyridine-dicarboxylic acids. Influence of the polarisation, polarizability, zwitter-ionic properties, and intra- and intermolecular hydrogen bonding of the ligands on stability of the  $\text{Eu}^{2+}$  ion and on position of the charge transfer band was considered. Possible mechanisms of the charge transfer from ligands to metal ions are discussed.

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## Analysis of $\text{Eu}^{3+}$ emission from different sites in $\text{Lu}_2\text{O}_3$

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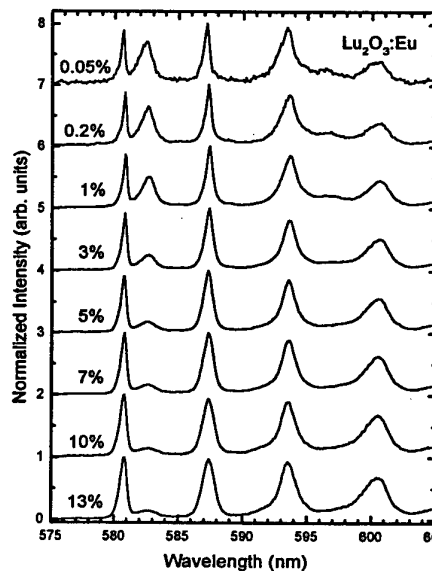
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$\text{Lu}_2\text{O}_3$  is a valuable host material for various activators. Its crystallographic structure is of the same type as  $\text{Y}_2\text{O}_3$ , a known host lattice for efficient, commercial phosphors. As in the case of yttria, the lutetia host lattice offers two crystallographic sites for the dopant ions. One of the sites has  $C_2$  symmetry, and the environment of the other possesses  $S_6$  ( $C_{3i}$ ) symmetry. 75% of the Lu ions are located in the  $C_2$  sites and 25% in the  $S_6$ .

Most of the emission appearing under non-selective excitation, for example into the charge-transfer band around 250 nm, results from the europium ions located in the  $C_2$  surroundings. This results from the fact that transitions within  $\text{Eu}^{3+}$  ions located in the  $S_6$  site are strongly forbidden as the electric dipole transitions. Considering the emission and absorption transitions within the 4f levels, for  $\text{Eu}^{3+}$  in  $S_6$  site only the  $^5D_0 \rightarrow ^7F_1$  emission and  $^7F_0 \rightarrow ^5D_1$  absorption is possible as weak magnetic dipole transition. In contrary, all the intraconfigurational transitions of Eu ions in the  $C_2$  site are allowed as electric dipole transitions.

In this communication we report and analyze the emission and energy transfer processes between Eu ions located in the two different sites. Site selective spectroscopy allowed us to selectively excite the dopants positioned in the different sites. We shall report the lifetimes of  $\text{Eu } ^5D_0$  level for ions located in the  $C_2$  and  $S_6$  environment. We will also analyze the transfer processes between the  $\text{Eu}^{3+}$  ions located in the two crystallographic sites. We will show that energy from the  $\text{Eu}^{3+}$  ions placed in the  $S_6$  site can be transferred to the ions in the  $C_2$  site. Concentration dependence of the transfer rate will be reported and analyzed. Continuous and pulsed excitation was used to analyze the various spectroscopic processes in which europium ions located in the different sites are engaged. Significantly different lifetimes of the emissions from the two sites allowed separating the luminescence from the  $S_6$  symmetry from this of the  $C_2$ .



Concentration dependence of emission spectra of  $\text{Lu}_2\text{O}_3:\text{Eu}$ . The band around 582.6 nm results from  $^5D_0 \rightarrow ^7F_1$  transition of  $\text{Eu}^{3+}$  in  $S_6$  site. Its intensity decreases with Eu-concentration due to energy transfer from this (higher-lying) site to the  $C_2$  site.

## Sintering properties of $\text{Lu}_2\text{O}_3$ -based luminophors for X-ray detection

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Lutetium-based phosphor materials are of increasing interest recently as potential ionizing radiation detectors. What makes them especially attractive for such applications is their high density and high Z-number of Lu. Combination of these two parameters makes Lu-containing luminophors very efficient in stopping high-energy ionizing radiation, which allows for using relatively thin layers of the phosphors [1, 2]. The research already resulted in finding interesting phosphors, among which Ce-doped  $\text{Lu}_2\text{SiO}_5$  (LSO) and  $\text{LuAlO}_3$  (LuAP) appear the most promising for PET-cameras in medical imaging.

Simple lutetium oxide,  $\text{Lu}_2\text{O}_3$ , was also found to be potentially attractive for commercial uses. Its very high density ( $\sim 9.4\text{g/cm}^3$ ) makes its stopping power for ionizing radiation of exceptional value. The energy of valence-to-conduction band gap is high enough [3, 4] to accommodate emitting levels of many activators, for example Tb, Eu, Tm, Dy. Unfortunately, excited states of Ce fall into the host conduction band, which prevent the dopant from producing of its fast d-f emission. Nevertheless, activation with many other ions is possible and their luminescence in this host can be observed.

In this communication we present the results of our research on sintering behavior of  $\text{Lu}_2\text{O}_3$  powders prepared with various synthesis techniques. The stress will be put on sintering properties of nanoparticulate powders of lutetium oxide made with combustion synthesis using urea or glycine as fuels engaged in reaction with  $\text{Lu}(\text{NO}_3)_3$ . It will be shown how the starting powders morphology influence their susceptibility for sintering. The influence of intentionally incorporated admixtures on sintering peculiarities will be discussed. Pictures of TEM and HRTEM of the starting powders and the final products will be presented to show the connection between the morphology of starting powders and the final products.

Finally, some spectroscopic properties of the starting powders and produced of them sintered ceramic samples will be shown. Among others, concentration quenching for Eu-doped powders and sintered pellets will be determined.

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## Preparation and energy transfer of $\text{Y}_2\text{O}_3\text{:Tb, Eu}$ nanophosphors

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The  $\text{Y}_2\text{O}_3\text{: Tb, Eu}$  nanophosphors were prepared in our laboratory by the combustion method for the optimal concentration of rare earth ions RE (Tb+Eu) 5 mol%, with the mole ratio of Eu/Tb are 7/3, 8/2 and 9/1. The optical properties such as luminescent spectra and decay times were measured in order to study the energy transfer between Tb and Eu. The effect of concentration as well as influence of annealing temperature were investigated. The luminescent intensity is maximum in the case of  $(\text{Y}_{0.95}\text{Eu}_x\text{Tb}_y)_2\text{O}_3$  nanophosphors ( $x+y=0.05$ ,  $x/y=8/2$ ) annealing 600°C, 30 minute is due to energy transfer between Tb to Eu. The lifetimes of the  $^5\text{D}_0\text{--}^7\text{F}_2$  transition of Eu at about 612 nm are 940  $\mu\text{s}$ , 650  $\mu\text{s}$  and 360  $\mu\text{s}$  for the mole ratio of Eu/Tb 9/1, 8/2 and 7/3 respectively. The lifetimes of Tb ( $^5\text{D}_4\text{--}^7\text{F}_j$ ) 545 nm are 400  $\mu\text{s}$  and 175  $\mu\text{s}$  for the ratio of Eu/ Tb 9/1 and 8/2 respectively. The energy transfer in the samples annealing 600°C is stronger than that in the samples annealing 700°C. The size effect will be investigated in order to determine optimal condition for prepare nanophosphors.

## Power dependence of emission spectra of Er and Yb co-doped LiNbO<sub>2</sub>

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The Stokes and anti-Stokes emission spectra of Er and Yb codoped LiNbO<sub>3</sub> crystal were recorded using a diode laser 980 nm and an excimer laser 308 nm as the excitation sources. The effect of excitation power on intensities of Stokes emission and anti-Stokes up-conversion emission were investigated. It was found that the Stokes emission intensity demonstrated a sublinear dependence on excitation power whereas the anti-Stokes emission lines a quadratic dependence.

The brief discussion of mechanisms responsible for this behaviour is presented.



**Undoped and Nd<sup>3+</sup>-doped nanocrystalline Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> ceramics spectroscopy.  
New laser properties and high-order stimulated raman scattering**

**A.A. Kaminskii, K. Ueda, H.J. Eichler, J. Lu, H. Yagi, T. Yanagitani, T. Murai,  
G.M.A. Gad**

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**High efficient stimulated raman scattering in new  $k(3)$ -nonlinear glasses**

**A.A. Kaminskii, H.J. Eichler, H.J. Hulliger, R.B. Burkhalter, G.M.A. Gad**

**New laser and nonlinear-laser properties of undoped and  $\text{Ln}^{3+}$  doped cubic crystals  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  and  $\text{Bi}_4\text{Si}_3\text{O}_{12}$**

**A.A. Kaminskii, S.N. Bagaev, K. Ueda, H.J. Eichler, J. Hanuza, N.V. Kravtsov,  
Ya, V. Vasiliev, J. Lu, N.I. Ivannikova, P. Reiche, G.M.A. Gad**

## Spectroscopic investigation of porphyrins and Ln(III) porphyrins

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Upper emission excited-state has been observed for variety of diamagnetic metal porphyrins. In the paramagnetic systems emission depends on the position of CT, d-, and f- excited states which take part in the porphyrin emission quenching.

Characteristic Q and S (Soret) bands of metal porphyrins in the visible region are assigned to excited S<sub>1</sub> singlet and the second excited S<sub>2</sub> states. Recently we have reported the absorption, IR and Raman spectra of porphyrin and Tb(III) porphyrin in solid and solution. Spectroscopic investigation have been done at room temperature. Correlation of the spectroscopic results in solids and solutions was made and the role of solvent molecules in modifications of the structure of porphyrin complex in solutions was considered.

Now we present spectroscopic investigation of new types of water soluble porphyrins (PP(Ser)<sub>2</sub>(Arg)<sub>2</sub>, their interaction with lanthanide ions (Pr, Eu and Yb) as well as emission of H<sub>2</sub>TPP porphyrin and TPPTb(III)acac compound. The relation of the intensity of the porphyrin emission on oxygen concentration in solution as well as energy of the excitation beam were studied. It was found that efficiency of emission depends on Ln(III) ion concentration in solution. The observed phenomenon is analyzed and the mechanisms of the excited states dynamics are considered.

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# W.L.ELECTRONICS

## BRUKER - SERVICE



### NMR

- Research spectrometer  
High Resolution 200-900 MHz  
Solid State WB 200-750 MHz
- Superconducting magnets up to 900 MHz
- Microimaging, Biospec

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- Electromagnets, power supplies
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- Spectrometers with spectral range from  
5  $\text{cm}^{-1}$  to 50 000  $\text{cm}^{-1}$   
and resolution up to 0.0015  $\text{cm}^{-1}$
- IR accessories
- FT-Raman spectrometers, microscopes IR,  
raman microscopes
- GC, TGA units

### QA/QC

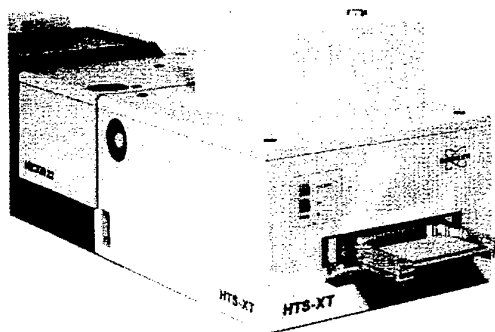
- FT-NIR spectrometers
- mini EPR spectrometers
- mini NMR spectrometers



*In 2000 year two Bruker optics products were honored R&D awards: MATRIX (industry FT-IR spectrometer) and IFS 28/B MICRO-ID (microbial identification system). The awards are given by R&D Magazine to recognize the 100 most technological significant new products of year. The awards is calling "The Oscars of Invention".*

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## Micro Titer Plate Accessory and Gilson 215 Autosampler.



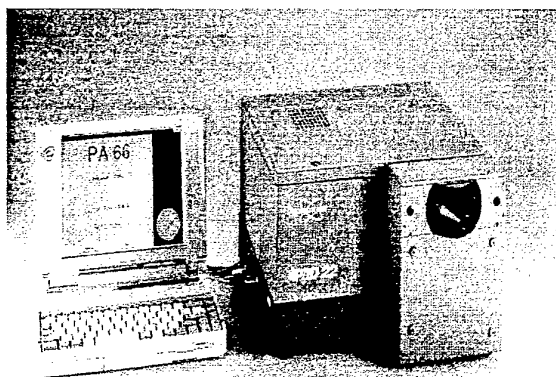
Bruker Optics has introduced an exciting new accessory for automated analysis of samples directly from micro titer plate. The HTS-XT (High Throughput Screening Extension) can analyze samples in either transmission or diffuse reflectance mode using 96, 384 and 1536 well plate formats. OPUS-NT software conducts batch manipulation of the two-dimensional data sets. The results can be presented as color contour maps to aid in visualization of concentration gradients or component distribution within the sample plates. The accessory is ideal for laboratories that have high sample throughput requirements. Applications include drug screening, analysis of biological fluids, combinatorial chemistry and synthesis control.

In addition to the new HTS-XT autosampler, Bruker Optics now offers integrated support of the Gilson 215 Autosampler system. The Gilson 215 autosampler is directly controlled by OPUS-NT software. Customized applications can be developed using the OPUS-NT VB Script and Visual Basic macro capabilities. The system can be used for almost all types of liquid analysis and can also serve to provide sample conditioning for micro plates. Features include:

- uses 96 and 384 wells
- flow rate: 120 ml/min
- compatible with FTIR, FT-NIR,  
FT-Raman flow cells
- 24 hour system operation.



## Polymer Identification System P/ID 22



P/ID 22 is compact and portable mid-infrared Fourier-transform spectrometer for the rapid and reliable identification of technical plastics by reflectance measurements. P/ID 22 provides rapid identification of colored, colorless, black or highly filled technical plastics and commercial polymers on basis of stored reference spectra. Reference data contains 30 polymer classes (more than 150 plastic samples) of blends, filler material and foams. The library can be easily extended by customer-specific polymers.

The system consists of stable and sealed optic and fast PC data system with an easy-to-use analytical software.

## RAPID 22 - Remote Air Pollution Infrared Detector

The Bruker RAPID 22 is a broadband infrared detection system for remote sensing of hazardous atmospheric compounds. The system performance allows real-time field screening analysis (analysis less than 1 s). The lightweight system includes an infrared radiation analyzer based on the proven Bruker ROCKSOLID™ interferometer. Internal calibration sources provide self-test and self-calibration for radiometric measurements. Due to the novel design of the sensor module, the system is resistant to mechanical shocks, vibrations and temperature extremes. It is hardened for field operations in harsh environments.

**Passive Remote Detection** is necessary if rapid, mobile and easy operation are needed. Typical applications include:

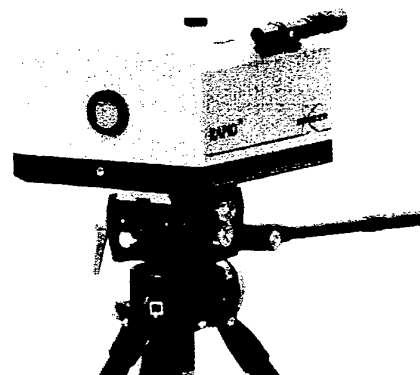
- Reliable identification of emitted industrial hazardous gaseous compounds,
- Observation of stack gas plumes, wildfires, etc.
- Remote sensing of aircraft emissions

The characteristic infrared "fingerprint" signatures of chemical agents are detected and identified by the RAPID 22. Sophisticated software avoids false alarms and discriminates against possible interferents. Due to the compact design and intuitive software, no special operator training is required.

If the highest sensitivity and quantitative results are needed, the **Active Setup** of the RAPID 22 fulfills these requirements. In the active configuration the sensor module (receiver) is permanently or temporarily aligned to an infrared source (transmitter) at a variable distance (typically 100 – 200 m). Current applications include:

- Ambient air measurements
- Control of diffuse emissions of waste disposals
- Fence-line monitoring
- Surveillance of waste disposal facilities
- Process control

For both configuration, active and passive, specially designed applications software for multi-component analysis is available and can be modified to the individual customer applications.



## Spectroscopy of fluorindate glasses doped with $\text{Sm}^{3+}$ ions

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Fluorindate glasses are perspective materials for IR-optics due to their low phonon energy ( $\sim 510 \text{ cm}^{-1}$ ). Numerous studies of spectroscopy properties of rare earth ions in these glasses have been performed (for references, see [1]). The aim of the report is to give preliminary results on the spectroscopy of fluorindate glasses doped with  $\text{Sm}^{3+}$  ions.

Fluorindate glasses in the following compositions  $(40-x)\text{InF}_3-20\text{ZnF}_2-20\text{SrF}_2-16\text{BaF}_2-2\text{GdF}_3-2\text{NaF}-x\text{SmF}_3$ , with  $x=1.0, 1.5, 2.0, 2.5, 3.0$  and  $3.5 \text{ mol } \%$  were prepared in a dry box, under an argon atmosphere [2,3]. Absorption spectra at room temperature were obtained in the spectral range from 340 to 2700 nm. To describe the experimental data on the oscillator strengths  $f_{\text{exp}}$  the following techniques were used: standard Judd-Ofelt approach (weak configurational interaction) [4,5] and two approaches [6-8] taking into account the dependence on energy of manifolds and the effect of electron correlation. Some spectroscopy parameters: radiative lifetime  $\tau_r$ , transition probabilities  $A_{JJ'}$  between multiplets and branching ratio,  $\beta_{JJ'}$  were calculated.

### Acknowledgments

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**New self-frequency conversion phenomena in  $\chi(2)$  and  $\chi(3)$  nonlinear-laser insulating crystals and their applied aspects****A.A. Kaminskii**

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In the last several years self-frequency conversion effects in  $\chi^{(2)}$ - and  $\chi^{(3)}$ -active undoped and doped (lasing) insulating crystals is an extensive growing area in laser and solid-state physics, as well as in modern optical material science. Such nonlinear processes as the self-frequency doubling (FD), self-stimulated Raman scattering (SRS), self-sum and –difference frequency mixing (SFM and DFM), and other opened widespread ways for creation of new type solid-state laser sources, including all-solid-state lasers and converters, which can generate in specific and otherwise hard to reach wavelengths in the very wide spectral range, covering the eye-safe and mid-IR atmospheric window regions. The report aims to provide an overview of some important steps of the problem. The talk will begin with historical aspects and some fundamentals, leading to a short review of the current state of the self-frequency conversion (FC) technology. Advanced trends will also be discussed, as well as some properties of novel self-FC lasers will be reviewed. In particular, among them will be briefly considered self-FD, –SFM, and –DFM lasers with undoped and doped acentric crystals  $\beta$ -LaBGeO<sub>5</sub>,  $\beta'$ -Gd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, Ba<sub>2</sub>NaNb<sub>5</sub>O<sub>15</sub>, Bi<sub>4</sub>Ge<sub>4</sub>O<sub>12</sub>, NaClO<sub>3</sub>, Sr<sub>0.6</sub>Ba<sub>0.4</sub>(NbO<sub>3</sub>)<sub>2</sub>, Ca<sub>4</sub>Gd(BO<sub>3</sub>)<sub>3</sub>O, as well as disordered crystals with the Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>4</sub>O<sub>14</sub> type structure, and self-SRS converters on the basis of  $\alpha$ -KGd(WO<sub>4</sub>)<sub>2</sub>,  $\alpha$ -KLu(WO<sub>4</sub>)<sub>2</sub>, PbWO<sub>4</sub>, PbMoO<sub>4</sub>, YVO<sub>4</sub>, GdVO<sub>4</sub> and other doped with Nd<sup>3+</sup>, Pr<sup>3+</sup>, and Yb<sup>3+</sup> ions, as well as the first results on self-frequency tripling (FT) and SFM in tetragonal  $\chi^{(3)}$ -active rare-earth vanadates.

A major part of these results were obtained by a cooperation of the author with Professors S.N.Bagaev, F.A.Kuznetsov, K.S.Alexandrov, J.Hanuza, J.Fernandez, J.Garcia-Sole, H.J.Eichler, K.Ueda, J.Hulliger and their co-workers within the Joint Open Laboratory for Laser Crystals and Precise Laser Systems, where main grant sponsors were the Russian Foundation for Basic Research and the Russian State Scientific Programs „Fundamental Metrology“, „Optics. Laser Physics“, and „Fundamental Spectroscopy“.